Research Program

Environmental Remediation and Water Resources Program

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The key driver for the Environmental Remediation and Water Resources Program (ERWR) within ESD is to provide the scientific foundation needed to guide the management of our shallow subsurface contaminants and resources. Over the last decade, it has become increasingly clear that if we are to face the environmental and water challenges of the future, we must view the earth as a complex system, one that includes many components that are coupled and highly dynamic over various spatial and temporal scales.

The DOE is responsible for the environmental health of over 140 waste sites across the United States, created from the production and testing of nuclear weapons. Metals and many radionuclides pose particularly daunting remediation challenges for DOE at these sites because, unlike organic contaminants, they do not irreversibly degrade to benign products (or only do so through very slow radioactive decay). Because understanding the complexity of the subsurface systems is a prerequisite to successful stewardship at these waste sites, a significant fraction of the research within the ERWR program focuses on investigating, measuring, and predicting coupled physical, geochemical, and microbiological processes that govern contaminant fate and transport and that impact remediation efficacy.

The inability to accurately measure and predict water cycle phenomena hinders our ability to effectively inform water resources management and policy. Because adequate and clean water resources are particularly important for the vitality of water-stressed regions such as California, much of the water-resources research performed in the ERWR focuses on development of techniques and insights that will lead to better management of California water resources. In addition to State water issues, the DOE is responsible for promoting America's energy security, while at the same time protecting the environment—this necessitates water-related research. For example, as worries over the world energy crisis and climate change intensify, the link between such issues and water is becoming ever more apparent and is leading to various challenges. The energy demand for generating and distributing clean water is tremendous; so too is the water demand for generating conventional and sustainable energy and biofuels. Although water issues are currently only a small fraction of the ERWR research portfolio, we anticipate more emphasis on research in this area, as both energy and water needs continue to increase.

Brief descriptions of research advances within the Environmental Remediation and Water Resources Program are given below.

ENVIRONMENTAL REMEDIATION

ESD scientists participating in the ERWR conduct multidisciplinary environmental research using theoretical, characterization, modeling, and experimental approaches that range from the molecular to the field scale. The synergy offered by the ensemble of competencies within the ESD facilitates investigation of complex natural systems. Many of the projects within the ERWR are associated with one of the following five themes:

- Development of advanced approaches for characterizing and predicting subsurface biological, hydrological, and geochemical properties and processes at the molecular to field scales
- Improved understanding of mechanisms and rates associated with complex subsurface system processes
- Improved understanding of the impact of subsurface system complexity on contaminant distribution and remediation efficacy
- Development of a basis for in situ remediation, especially for metals and radionuclides that respond to redox manipulation and microbial community stimulation.
- Development of remote approaches for detecting and discriminating unexploded ordnance (UXOs)

ESD scientists within the ERWR program have recently developed novel approaches that can be used to characterize microbial properties and processes, and to monitor how they change in response to environmental perturbations. ERWR scientists have combined phylogenetic and functional gene arrays to identify mechanisms of chromium immobilization via biostimulation, and have demonstrated the impact of electron-donor supply on microbial community development. ERWR researchers have developed techniques for large-scale extremophile production needed for protein complex analysis. They have developed a community database and web application that permits exploration of microbial community structure relationships to disease states and environmental factors. Many of these studies were performed in collaboration with the Virtual Institute of Microbial Stress and Survival (VIMSS), which is based at Berkeley Lab and which seeks to identify stress-response pathways of microbes important for environmental remediation.

Through development of novel synchrotron and isotopic methods, ERWR scientists have quantified mechanisms and rates associated with contaminant transport and cleanup processes. Grazing incidence small angle x-ray scattering approaches have been used to elucidate the mechanism and kinetics of early environmental nanoparticle growth; synchrotron Fourier transform infrared methods have been used to explore iron biomineralization processes. Carbon isotopic compositions of dissolved methane and inorganic carbon were used to indicate the biodegradation potential in regions downgradient from a trichlorethene plume at the Idaho National Laboratory. ERWR researchers have used time-lapse sulfur isotopes to elucidate the timing and mechanism of sulfate reduction that occurred during bioremediation of a uranium-contaminated aquifer, and have used isotopic signatures to infer the origin of 99Tc in Hanford groundwater.

ERWR researchers have advanced the use of geophysical approaches for characterizing subsurface hydrogeological properties and for monitoring biogeochemical processes associated with remediation efforts. Spectral induced polarization and spontaneous potential methods were used to track the production of iron sulfides and the subsurface regions of active metabolism, respectively, during a local field-scale uranium biostimulation experiment. A stochastic framework was developed to permit the quantitative estimation of biogeochemical end-products using time-lapse geophysical datasets and petrophysical relationships. Development of analytical and numerical inversion approaches for interpreting complex, time-lapse conservative tracer breakthrough datasets both highlighted how biogeochemical products associated with remedial treatments can alter flow characteristics at the local field scale. Recognizing the need to provide quantitative information about subsurface properties and objects over plume-relevant scales, ERWR scientists have developed a framework for integration of multiscale hydrological data and have developed the Berkeley Unexploded-ordnance (UXO) Discriminator (BUD) field instrument that uses electromagnetic approaches. Their studies describe how BUD can differentiate (in real time) buried UXO from harmless metal and determine the location, size, and shape of such potential explosives. This instrument has won several accolades, including the 2007 "R&D 100" award for technology advances from *R&D Magazine*.

Laboratory and field studies conducted by ERWR scientists have revealed phenomena that have significant implications for contaminant transport and development of sustainable remediation strategies at many contaminated DOE sites. Column-profiling studies, designed to mimic the leakage of highly saline and alkaline radioactive waste solutions from Hanford storage tanks into sediments, revealed that the transport of uranium was strongly dependent on flow rate, and that conventional predictions based on equilibrium Kd partitioning of uranium would greatly underestimate the extent of plume migration. Column studies on sediments from the Oak Ridge National Laboratory Integrated Field-Scale Subsurface Research Challenges (IFC) site revealed that organic carbon-induced uranium reduction in sediments can exhibit rapid early stage reduction followed by transient uranium oxidation, and that the reoxidation can be facilitated by high concentrations of Fe(III). ERWR scientists have recently assessed the potential for immobilizing and detoxifying chromium-Cr(VI)-contaminated groundwater at the Hanford Site using lactate-stimulated bioreduction. Microbial, geophysical, and geochemical analysis of groundwater, coupled with stable isotope monitoring, permitted accurate tracking of microbial processes during this field treatabilty study. This study also confirmed that Cr(VI) was successfully removed from groundwater at the site and that concentrations of Cr(VI) remained below drinking water standards for several years after injection. Such studies reveal the benefits of interdisciplinary approaches for investigating and manipulating complex earth systems.

Several conceptual and numerical models have been developed to investigate contaminant transport and reactivity in natural and engineered environments. ERWR scientists have integrated the coupled effects of microbial Fe-oxide reductive dissolution, biogeneic sulfide production, and metal sorption through the use of a full-surface-complexation model under redox disequilibrium to develop insights about important biogeochemical processes that affect the cycling of metals in lacustrine environments. The fate and transport of tritium within a constructed underground beamline facility was documented using numerical solutions supported by laboratory studies and data analysis. This study identified the main mechanisms of tritium transport through the engineered and surrounding fractured rock environment, and can be used to implement beamline design changes or mitigation measures, if necessary.

WATER RESOURCES AND QUALITY

To optimally manage our water resources, ERWR scientists are developing insights about the flow and transport of water and nutrients through natural systems. With a population of over 30 million people, an agricultural economy based on intensive irrigation, and large urban industrial areas, California is highly dependent on water for its vitality and productivity. Although the majority of the water research performed in ERWR is focused on California systems, the insights and approaches developed are expected to be generally transferable.

The Berkeley Water Center has been developed to bring together expertise at LBNL and UCB to tackle complex water problems and their impacts on biological, economic, agricultural, and other systems. The Berkeley Water Center Digital Watershed is a portfolio of projects that combine engineering, computer science, ecological, and hydrometerological expertise to advance our ability to interrogate and optimally manage water systems. A Microsoft-sponsored eScience project within this portfolio has created the cyberinfrastructure necessary to connect disparate databases and analysis tools, facilitating the synthesis of data acquired across the Ameriflux and FLUXNET observatories to address carbon science questions.

ERWR scientists have also developed a mechanistic model that couples hydrology, nutrient cycling, and vegetation responses. They have used this model to investigate N cycling and losses from agricultural fields, as well as to explore the effects on N cycling of irrigation and fertilizer parameters. Understanding NO, N_2O, and CO_2 emissions from the soil surface to the atmosphere is a necessary prerequisite to controlling greenhouse gas emissions. Development of such insights and modeling capabilities are increasingly necessary in light of increasing production of biofuels, food, and fiber production.

System-level studies have been carried out to characterize and understand complex hydrological and ecological phenomena that impact water resources and quality. Using spectral and shape characteristics from high-resolution remote sensing imagery and statistical discrimination approaches, ERWR scientists created maps of moist-soil wetland vegetation in the San Joaquin Basin, which can be used to assess seasonal evapotranspiration as needed for improving wetland-drainage management approaches. The Grassland Ecological Area within the San Joaquin Basin provide significant habitat to water fowl, although the water quality of the San Joaquin River is threatened by drainage from the salt, boron, and nutrient-rich wetlands. Through studying three matched pairs of wetland basins within a California Ecological Area, the impact of delayed wetland drainage on aquatic biota and water quality was established. Such studies can be used to guide the timing (and thus dilution) of wetland drainage to the river, with a goal of minimizing the impact on ducks and shorebirds.

The impact of climate on groundwater level was numerically investigated through two studies. Using 15 km grid cell resolution, an ERWR study documented the correlations between the water table within the Merced River Basin and precipitation, snow water equivalent, temperature, runoff, and evaporation as a function of season. The study illustrated that the correlations varied as a function of season, and that the strongest correlations were in the spring, when the interaction of land-surface and atmospheric processes were most active. Another study was performed to assess the impact of drought within the entire Central Valley of California from the period of 2010–2070. The study found that under the most severe drought scenarios, stream flow to major California reservoirs was reduced to 70% below average and that surface irrigation deliveries to agriculture fell to 50%. Geographical comparisons of the simulations suggested that the northern Central Valley is better protected from drought than the southern region.

ERWR TECHNICAL ASSISTANCE

ERWR continues to be the Environmental Remediation Sciences Program (ERSP) Office for the Office of Science. The ERSP Office maintains the dynamic ERSP Web home page (www.lbl.gov/ERSP/) with links to investigators, program element managers, science team leaders, recent publications, annual meeting registration, calls for proposals, review documents, and other Web sites. In addition, the ERSP Office also organizes the ERSP annual investigators meeting, with more than 150 participants and sessions for posters, presentations, and breakout sessions.

ERWR scientists also manage the Environmental Program at the Advanced Light Source (ALS), as described by http://esd.lbl.gov/ALS_environmental/index.html. This program is designed to assist environmental researchers in gaining familiarity with and access to the ALS, and in assisting with environmental investigations at the ALS. Many of the environmental investigations in this program focus on understanding how and what microbiological and geochemical species are distributed relative to contaminants and within natural geological materials, which processes occur, and the rates at which they occur. With funding from ERSP, this program has provided support across four beamlines, providing a range of measurement support scales from nanometers to centimeters.

SPONSORSHIP

ERWR receives the majority of its support for environmental research from DOE programs in the Office of Science, Office of Biological and Environmental Research. These programs include the Environmental Remediation Sciences Program (ERSP) and the Genomics: GTL Program. DOE's Office of Environmental Management has supported some of the DOE site-specific studies. Research associated with unexploded ordnance is supported by the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense. NSF supports the collaboration of ERWR scientists with university researchers. Many of the water quality projects were supported by the State Water Resources Control Board, the U.S. Bureau of Reclamation, the UC Salinity/Drainage Program, and LBNL Laboratory Directed funds. Studies exploring the impact of climate and groundwater were supported by the California Energy Commission. Support for ERP projects is also provided by NASA, SERDP, Cal-EPA, other DOE Labs, the Sonoma County Water Agency, U.S. Army, and the U.S. Bureau of Land Management.

Comparative Analysis of Microbial Composition During Field-Scale Chromium Bioremediation

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RESEARCH OBJECTIVES

During a field-scale chromium treatability study at the Department of Energy Hanford 100-H site, WA, a single dose of a slow-release electron-donor hydrogen-release compound (HRC) was applied to a contaminated aquifer to stimulate microbial reductive precipitation of hexavalent chromium Cr(VI). Here, we present an analysis of microarray-based prokaryotic population dynamics and correlations with geochemical observations following this application over two years.

APPROACH

A high-density 16S rRNA phylogenetic microarray (PhyloChip) and a functional gene array (FGA) were used to analyze groundwater samples from multiple depths in injection and monitoring wells taken at intervals pre- and post-HRC injection. Following filtration, genomic DNA was extracted and polymerase chain reaction (PCR) amplicons or MDA-amplified community-DNA were analyzed by microarray hybridization. A range of geochemical and geophysical parameters were also monitored.

ACCOMPLISHMENTS

Following HRC injection, reducing conditions had rapidly established with a corresponding decline in DO, Eh, and nitrate. Cr(VI) concentrations declined steadily over 6 weeks and remained below upgradient concentrations. Microbial biomass was stimulated by two orders of magnitude (Figure 1a). PhyloChip data demonstrated depth-stratified microbial communities with temporal shifts in composition corresponding with observed geochemistry. A sustained enrichment of iron (Figure 1c) and sulfate reducing bacteria (Figure 1b) was observed, suggesting indirect chromium immobilization through interaction with reactive iron or sulfide by-products. Nitrate reducers such as *Pseudomonas* also remained elevated over the two years, and FGA array data demonstrated a sustained enrichment of *Pseudomonas* chromate reductase genes, suggesting that direct reduction of chromate may also be significant in chromium immobilization. Based on this data, organisms representing each of these functional groups have been isolated and characterized.

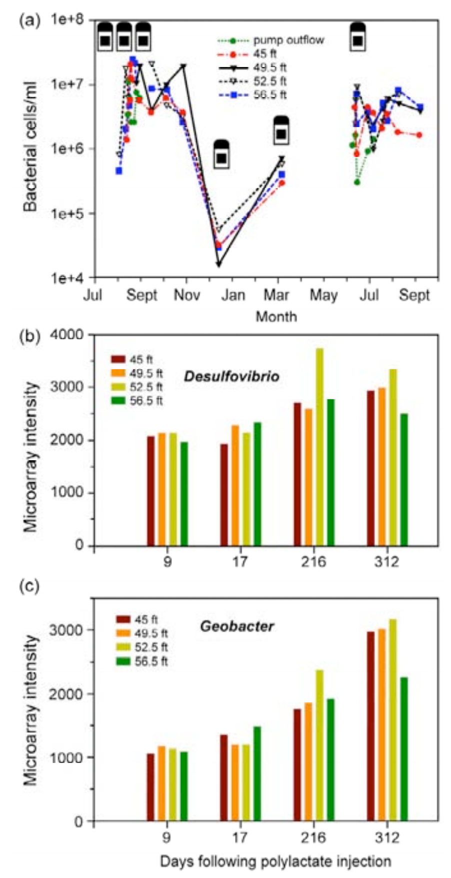

Figure 1. (a) Enrichment of microbial cells in Hanford groundwater following polylactate injection; (b) PhyloChip microarray intensity for sulfate-reducing *Desulfovibrio* spp. following polylactate injection; (c) PhyloChip microarray intensity for iron-reducing *Geobacter* spp. following polylactate injection.

SIGNIFICANCE OF FINDINGS

The combination of phylogenetic and functional gene arrays represents a complementary high-throughput approach to elucidating mechanisms responsible for contaminant immobilization in the subsurface. In this study, we used this approach to identify the microorganisms contributing to both direct and indirect mechanisms of chromium immobilization at the Hanford 100-H site, following a single-injection of polylactate electron donor.

RELATED PUBLICATIONS

DeSantis, T.Z., E.L. Brodie, J.P. Moberg, I.X. Zubieta, Y.M. Piceno, and G.L. Andersen, High-density universal 16S rRNA microarray analysis reveals broader diversity than typical clone library when sampling the environment. Microb. Ecol. 53, 371–383, 2007.

Brodie, E.L., T.Z. DeSantis, Y.M. Piceno, and G. L. Andersen, High-density DNA microarray analysis for monitoring microbial community composition and dynamics. In: Molecular Microbial Ecology Manual. 3rd edition, G.A.Kowalchuk, ed., Kluwer Academic Publishers, Amsterdam, The Netherlands, 2007.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Influence of Electron Donor Type and Concentration on Microbial Population Dynamics During Uranium Reduction and Remobilization

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RESEARCH OBJECTIVES

Enhanced reductive precipitation of U(VI) through stimulation of indigenous microorganisms is an attractive, low-cost strategy for *in situ* remediation of contaminated groundwaters and sediments. However, our previous long-term column studies demonstrated that after an initial period of U(VI) reduction and immobilization, reoxidation of U(IV) and remobilization of U(VI) occurred. The rate of organic carbon (OC) supply determines not only the amount of electron donor available for bioreduction of U(VI), but also affects the resulting concentration of aqueous (bi)carbonate generated by microbial respiration. Increased (bi)carbonate concentrations drive aqueous U(VI) concentrations to higher levels through formation of stable U(VI) carbonato complexes, including $Ca_2UO_2(CO_3)_3$(aq), and make U(IV) oxidation under reducing conditions favorable. We are currently investigating the effects of various OC forms and supply rates on the long-term stability of bioreduced U, and on the dynamics of the resulting microbial communities in relation to U redox changes.

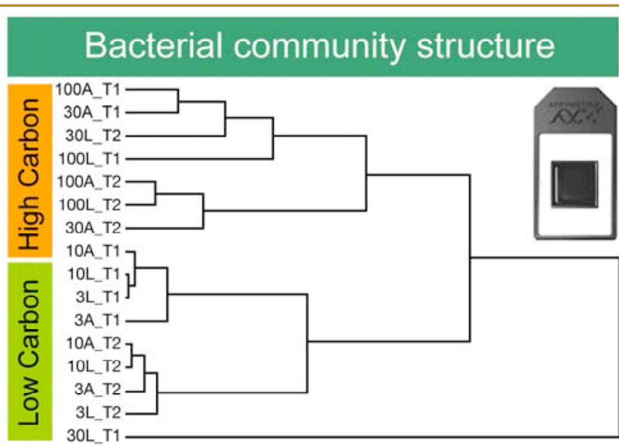

Figure 1. Hierarchical cluster analysis of PhyloChip microarray data showing electron donor (OC) concentration as the major factor distinguishing bacterial community composition. Numbers correspond to carbon concentration (3, 10, 30, 100 mM), L = lactate, A = acetate, T1 = sample taken during reduction phase in high OC columns, T2 = sample taken during re-oxidation phase in high OC columns.

APPROACH

Our current studies are being conducted using historically U-contaminated sediments from Area 2 of the Field Research Center, Oak Ridge National Laboratory, in flow-through columns. Microbial communities were stimulated by the addition of OC supplied as either acetate or lactate at four different concentrations (100 mM, 30 mM, 10 mM, 3 mM OC equivalents). Columns were sampled at two time points. In the columns receiving 100 or 30 mM OC, the time points correspond to a phase of net U-reduction and a later phase of U(IV) reoxidation and U(VI) remobilization. DNA was extracted from columns, 16S rRNA genes were amplified, and the microbial composition was analyzed using a high-density phylogenetic microarray (PhyloChip).

ACCOMPLISHMENTS

It was observed that lactate and acetate supplied at equivalent rates have a similar impact on uranium mobility with higher OC, resulting in re-oxidation of U(IV) after an initial period of U(VI) reduction. Similarly, it was demonstrated that organic carbon (OC) supply rate, not OC form, had the largest impact on microbial community structure (Figure 1). The diversity (richness) of bacterial and archaeal communities increased over time, with those receiving the fermentable OC form (lactate) having higher initial richness. Closer examination of the bacterial community composition demonstrated the presence of known metal/U-reducing bacteria in all columns at all time points; however, the dynamics of these organisms varied with both organic carbon supply rate and form.

SIGNIFICANCE OF FINDINGS

This data demonstrates that the initial rate of electron donor supply during heavy metal remediation strongly impacts microbial community development. Uranium remobilization occurred irrespective of electron donor form, and occurred despite the presence of multiple species of metal-reducing bacteria.

RELATED PUBLICATIONS

Brodie, E.L., T.Z. DeSantis, D.C. Joyner, S. Baek, J.T. Larsen, G.L. Andersen, T.C. Hazen, D.J. Herman, T.K. Tokunaga, J.M. Wan, and M.K. Firestone,Application of a high-density oligonucleotide microarray approach to study bacterial population dynamics during uranium reduction and reoxidation. Appl. Environ. Microbiol. 72, 6288–6298, 2006.

Wan, J. M., T.K.Tokunaga, E. Brodie, Z.M. Wang, Z.P. Zheng, D. Herman, T.C. Hazen, M.K. Firestone, and S.R. Sutton, Reoxidation of bioreduced uranium under reducing conditions. Environ. Sci. Technol., 39, 6162–6169, 2005.

ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, Environmental Remediation Sciences Program (ERSP), of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Spatial Characterization of the Bacterial and Archaeal Community Structure in the Passalid Beetle Gut

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RESEARCH OBJECTIVES

Understanding the microbial processes by which wood-ingesting insects derive energy may aid large-scale conversion of lignocellulosic biomass into biofuel. We examined the prokaryotic biome of the wood-eating passalid beetle, *Odontotaenius disjunctus,* with a 500,000-probe PhyloChip targeting multiple unique regions of the 16S rRNA gene. This passalid beetle has developed a symbiotic relationship with microbes to survive on a low-nitrogen diet that requires microbial-community-derived enzymes to digest the complex polysaccharides and lignins of plant cell walls. The adult gut of this approximately 3 cm beetle is over 10 cm in length and consists of four morphologically distinct sections, the foregut (FG), midgut (MG), anterior hindgut (AHG), and posterior hindgut (PHG). The fungal composition of these gut regions has been extensively studied, and microscopy has demonstrated a morphologically diverse bacterial population in the hindgut. Relatively little, however, is known about the bacterial or archaeal diversity, which likely contributes key enzymes for lignocellulose processing, in addition to fixing atmospheric nitrogen for host nutrition.

APPROACH

To perform an in-depth census of the prokaryotic composition of each gut region, we used a high-density (500,000-probe) 16S rRNA microarray (PhyloChip) to screen for the presence and relative abundance of most known prokaryotes in a massively parallel assay. Living passalid adults were fed fresh hardwood chips for over one month before aseptic dissection of the gut and separation into the four sections. Sections were preserved and nucleic acids extracted from gut homogenates. Bacterial and archaeal 16S rRNA genes were amplified separately. The amplified products for each sample were quantified, pooled, fragmented, biotin-labeled, and hybridized for 16 h to the PhyloChip.

ACCOMPLISHMENTS

Analysis of bacterial composition demonstrated that across the same gut region, composition was highly similar across multiple individuals, while most gut regions were distinct. The AHG had the most unique composition, with higher relative abundance of clostridia, Bacteroidetes, sulfate reducers, and potentially nitrogen-fixing spirochetes. The AHG was the only location where methanogens were detected. Earlier microscopic work has shown that bacteria in this section form a solid surface biofilm. By contrast, the MG and PHG from individual beetles clustered tightly and contained higher proportions of alpha-proteobacteria and lactobacilli.

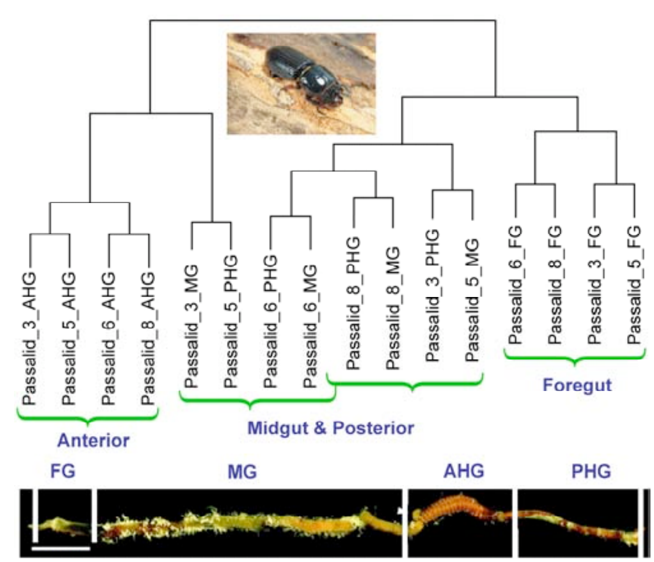

Figure 1. Hierarchical cluster analysis of PhyloChip microarray data demonstrating the compartmentalization of microbial populations within the passalid beetle gut

SIGNIFICANCE OF FINDINGS

This study represents the first comprehensive view of the passalid beetle gut bacterial and archaeal population. It has revealed a diverse community that is compartmentalized in terms of composition and likely function. The co-occurrence of anaerobic and aerobic processes within gut regions suggests existence of oxygen and/or hydrogen gradients along which microbial species partition themselves. This study represents the first steps to understand how these isolated populations, in one of nature's most efficient biorefineries, interact to deconstruct cellulosic materials.

ACKNOWLEDGMENTS

This work was partially supported by the National Science Foundation, Biodiversity Surveys and Inventories Program (DEB-0072741 and DEB-0417180) and REU supplements (to MB) and use of the LSU DNA sequencing facility was supported by a NSF Multi-user Equipment Grant (DBI-0400797). Part of this work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Berkeley National Laboratory, under Contract No. DE-AC02-05CH11231.

Large-Scale Production of Anaerobic Sulfate Reducers

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RESEARCH OBJECTIVES

The Virtual Institute for Microbial Stress and Survival (VIMSS, http://vimss.lbl.gov/) investigates stress response pathways in model organisms for the remediation of heavy metals and radionuclides in groundwater at DOE sites. The Protein Complex Analysis Project (PCAP, http://pcap.lbl.gov/), a subproject of VIMSS, focuses on high-throughput analysis of microbial protein complexes in the anaerobic, sulfate-reducing organism, *Desulfovibrio vulgaris* Hildenborough (DvH). Large volumes of culture of consistent quality are needed because of the relatively low cell density of DvH cultures (one order of magnitude lower than *E. coli*, for example) and PCAP's challenge to characterize low-abundance membrane proteins. In this summary, we describe our unique application of continuous flow fermentors to produce the large quantities of extremophile biomass required for PCAP.

APPROACH

Large-scale production of DvH presents several challenges. The organism is a metal reducer, and produces hydrogen sulfide, which is corrosive to the stainless steel parts of standard fermentors. Because the production volumes preclude working either in an anaerobic chamber or in a biosafety cabinet, we designed a benchtop system that could maintain anaerobic conditions and prevent contamination. Our facility has four 5-liter volume fermentors, which were custom-manufactured with nonmetallic wetted parts by Electrolab, UK. The fermentors are equipped with temperature and pH control, and redox-potential monitoring. To maintain anaerobic conditions, the fermentors are continuously sparged with nitrogen.

To improve culture consistency, we operate the fermentors in continuous flow mode. DvH is grown to late-mid-log phase (about 5×10^8 cells/mL) in batch mode, and then a lactate and sulfate-defined medium is applied at a dilution rate of 0.15 h^{-1} (0.6 L/h) to maintain the culture at a constant cell density. The prevailing redox potential during culture growth ranges from -500 to -700 mV. Once flow is initiated, the collected effluent is chilled to 4°C and held until the biomass is harvested by centrifugation. Cell density, which is directly correlated to optical density, is continuously monitored by pumping a recycle line through a cuvette in a small spectrophotometer (Ocean Optics, FL).

Figure 1 shows the optical density increase during batch phase, followed by its approach to steady state during continuous-flow phase. For reference, the OD of stationary phase DvH is 1. The total protein concentrations throughout the production range from 110 to 200 μg/mL. During continuous flow, approximately 35 to 55 mM of lactate and 5 to 15 mM of sulfate are consumed.

ACCOMPLISHMENTS

We have developed and optimized fermentor operation to produce large volumes of DvH, yielding reproducible, high-quality biomass for protein complex analysis. Running two fermentors in parallel, we are able to produce 100 L of culture per week. We have also developed analytical protocols to monitor consistency of production.

SIGNIFICANCE OF FINDINGS

Our methodology can be applied to produce a range of extremophile microorganisms under controlled conditions. Extremophiles have the greatest potential for remediating the most recalcitrant contaminants, and for the production of biofuels.

ACKNOWLEDGMENTS

We are grateful to Lauren Camp and Megan Shelby for assistance in the production runs and sample analysis. This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Genomics:GTL Program, of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

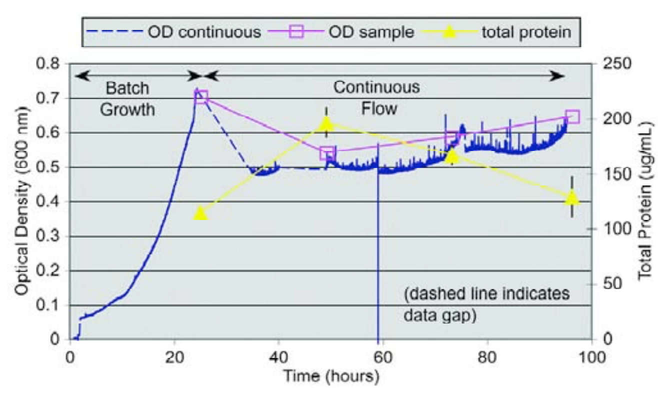

Figure 1. Data from a production run of DvH, grown at 30°C, in a 5 L customized fermentor. The optical density (OD) is directly correlated with cell density, and continuously monitored in the fermentor assembly.

Greengenes: Gene Database and Web Application for Microbial Ecologists

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RESEARCH OBJECTIVES

Diverse microorganisms living in the environment or within human tissues often act *in concert* to affect natural chemical cycling in the environment, as well as human health. In contrast to identifying single species' infections or searching for a single organism correlating with an environmental change, ecologists and medical researchers now analyze the entire microbial community structure and dynamics. This new research field has provided insights into medical problems such as obesity, inflammatory bowel disease, allergen sensitivity, periodontitis, vaginosis, pneumonia, and viral infection susceptibility. Environmental microbiologists have likewise found trends between microbial communities and the corresponding atmospheric conditions, groundwater redox potential, and soil moisture, as examples. The objective of the Greengenes project is to efficiently relate microbial community structure to disease states and environmental factors.

APPROACH

Presently, the bacterial and archaeal communities of the human biome and earth's biosphere remain mostly undefined, because most microorganisms have not been successfully grown (cultured) and studied in a laboratory. The advent of gene-based, culture-independent surveys and the availability and falling cost of high-throughput sequencing now allows inventories of all microbial community members. This has been accomplished most commonly using the 16S rRNA gene, a highly conserved and reliable marker for archaeal and bacterial species identification, and more recently using the ITS region of fungal genomes. Unfortunately, the ability to analyze and compare these data, and thereby make insights into the associated diseases, is impeded by a lack of high-quality, comprehensive databases and tools. Currently, researchers must independently surmount the same post-sequencing obstacles, namely: (1) making a reliable multiple sequence alignment (MSA) in order to compare sequences, (2) filtering out low-quality reference sequences from the public databases, (3) determining the identity of their sequences in the face of limited taxonomic classification of public sequences, (4) handling increasingly large datasets in an efficient manner, and (5) comparing overall community structure of their samples to public datasets. *This entire process has been simplified and standardized in the Greengenes web application.*

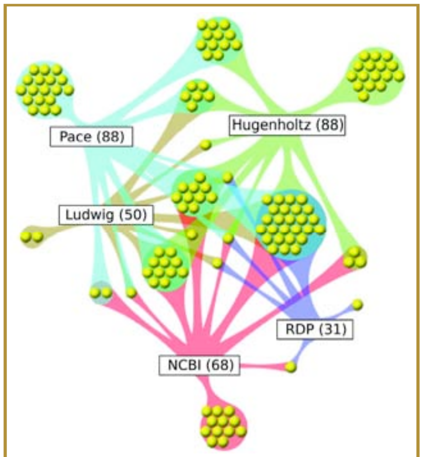

Figure 1. Classification terms shared among independent curators represented as a five-way Venn diagram. Yellow spheres represent the 126 Phyla or Candidate Division names encountered in at least one of the five taxonomy systems (Pace, Hugenholtz, Ludwig, RDP, or NCBI). Numbers in parentheses are the count of Phyla or Candidate Division names recognized by an individual curator. Clusters of yellow spheres connected by more than one colored web symbolize names recognized by multiple curators.

ACCOMPLISHMENTS

Greengenes has been implemented as a web application at http://greengenes.lbl.gov. It is the first resource to deconvolute the classification of microorganisms from both the environment and clinical material (Figure 1). It has become an internationally recognized resource, as evidenced by its frequent citations. Recently, it was used to demonstrate the effects of atmospheric pressure and temperature on urban bioaerosols at inhalation height, and to discover that salinity is the major factor influencing bacterial populations in aqueous environments.

SIGNIFICANCE OF FINDINGS

The Greengenes standardized methods for the analysis of community DNA data now allows research labs without dedicated bioinformatics support to determine factors affecting the types and quantities of microorganisms living in an environment. Continued usage of this service will be necessary for accurately analyzing the massive influx of 16S rRNA and ITS data and for sharing and comparing community structures from diverse samples. We anticipate this work will soon benefit clinicians making point-of-care decisions.

RELATED PUBLICATIONS

DeSantis, T.Z., P. Hugenholtz, N. Larsen, M. Rojas, E.L. Brodie, K. Keller, T. Huber, D. Dalevi, P. Hu, and G.L. Andersen, Greengenes: A chimera-checked 16S rRNA gene database and workbench compatible with ARB. Appl Environ Microbiol, 72, 5069–5072, 2006.

DeSantis, T.Z., P. Hugenholtz, K. Keller, E.L. Brodie, N. Larsen, Y.M. Piceno, R. Phan, and G.L. Andersen, NAST: A multiple sequence alignment server for comparative analysis of 16S rRNA genes. Nucleic Acids Res, 34, W394–399, 2006.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Genomics:GTL Program, of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

Development of a New Tool to Study Nucleation and Growth of Nanoparticles on Mineral Surfaces

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RESEARCH OBJECTIVES

The sorption, nucleation, and growth of nanoparticles on mineral surfaces may control the mineral surface's reactivity, and hence markedly affect aqueous metal contaminant transport and other surface-controlled reactions. Recently, grazing incidence small angle x-ray scattering (GISAXS) has been used to analyze the size, shape, and distribution of quantum dots and polymers on substrates. However, no work has been attempted thus far using GISAXS for *in situ* observations of environmental interfacial processes—such as the nucleation and growth or aggregation of nanoparticles on mineral surfaces. In this study, we (1) developed an *in situ* time-resolved GISAXS capability to allow real-time geochemical kinetics analysis of nanoparticle reactions at mineral-water interfaces; and (2) elucidated the mechanisms and kinetics of early nucleation and growth of important environmental nanoparticles.

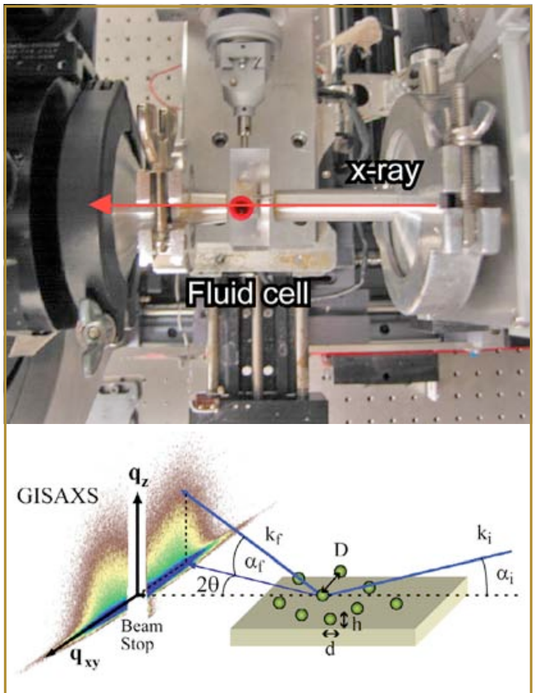

Figure 1. GISAXS setup allows us to observe the in situ real time early nuclei evolution (at nanoscale, a very short measurement time: seconds) of nanoparticles at mineral-water interfaces. D: particle distribution (spacing); h: height of nanoparticles; d: lateral size of nanoparticles; ki: incident x-ray; kf: scattered x-ray by newly formed nanophase.

APPROACH

We developed a new *in situ* time-resolved GISAXS capability that can be used either under dry or aqueous conditions. Using this setup, we investigated the kinetics and mechanisms of early nucleation and growth of iron oxide nanoparticles at water-mineral interfaces. In the experiments, the samples consisted of quartz substrates exposed to freshly prepared ferric solutions. By analyzing the simultaneous small angle x-ray scattering (SAXS) from the overlying solution and the GISAXS from the interface, we could extract the initial kinetics of nucleation and growth (numbers of nuclei and volume) and the morphological parameters (size, shape, and distribution) for both homogeneously (solution) and heterogeneously (interface) nucleated particles.

ACCOMPLISHMENTS

We investigated the initial nucleation and growth of iron oxide nanoparticles on quartz surfaces under different ionic strengths and aqueous iron concentrations (Figure 1). Utilizing simultaneous SAXS/GISAXS, we were able to distinguish the quantitative contribution between homogeneous and heterogeneous nucleation under different conditions. We found that ionic strength affects interparticle distances and particle sizes and shapes. At $[Fe^{3+}] = 10^{-4}$ M, heterogeneous nucleation was found to be more dominant and faster than homogeneous nucleation, whereas homogeneous nucleation is more important at higher $[Fe^{3+}]$ concentrations. This result is the first direct experimental evidence showing quantitative contributions caused by each mechanism at aqueous interfaces.

SIGNIFICANCE OF FINDINGS

In situ observations of the early nucleation and growth of nanoparticles in aqueous systems have been a challenging issue, because of (1) difficulties in distinguishing between homogeneous and heterogeneous nucleation processes; (2) difficulties in measuring the early stage kinetics, as a result of slow data acquisition and disturbance of the reaction system; and (3) small observation areas. By using an *in situ* time-resolved simultaneous SAXS/GISAXS, we were able to distinguish the quantitative contribution between homogeneous and heterogeneous nucleation without interrupting surface reactions. This technique also allows statistically improved real-time geochemical kinetics analysis of nanoparticle formation compared to other methods, and is highly complementary to imaging techniques such as atomic force microscopy or transmission electron microscopy.

RELATED PUBLICATION

Jun, Y.S., G.A. Waychunas, and B. Lee, Kinetic study of nucleation and growth of environmental nanoparticles at water-mineral interfaces using *in situ* time-resolved GISAXS. American Crystallography Association Series 2, 34, 52, 2007.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Environmental Science Program at the Advanced Light Source

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RESEARCH OBJECTIVES

The goal of the Environmental Science Program at the Advanced Light Source (ALS) is to further the research mission of OBER's Environmental Remediation Science Program (ERSP), by improving utilization of the ALS in the ERSP research effort, and generally increasing the quantity and quality of environmental research conducted at the ALS.

APPROACH

The ALS is a DOE national user facility with many unique spectroscopic and microscopic capabilities suited to application in environmental science. The program supports the research mission of ERSP by supporting ERSP PIs on research projects that can benefit from the resources at the ALS. These collaborations take many different forms, including participation in experimental design, novel sample cell development, data interpretation, beam time proposal writing, and data collection. The program specifically focuses on four beam lines at the ALS. These beam lines include BL 1.4.3-infrared spectromicroscopy, BL 8.3.2-x-ray micro-tomography, BL 10.3.2-x-ray microprobe and micro-x-ray diffraction, and BL 11.0.2-scanning transmission x-ray microscopy (STXM).

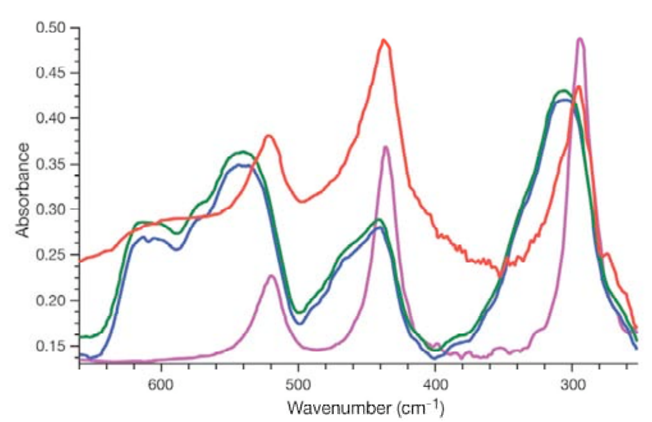

Figure 1. Synchrotron FTIR spectra of hematite with and without ferrihydrite before and after exposure to DIRB

ACCOMPLISHMENTS AND SIGNIFICANCE

In the past year, the program has worked with many different research groups for over 600 hours of beam time. Examples of these projects include: utilizing the Fourier transform infrared (FTIR) beamline (1.4.3) to study *in situ* iron biomineralization processes; imaging the pore-size distribution within synthetic aggregates using microtomography (8.3.2); examining the iron mineral transformations within those aggregates, using the micro-XAS capabilities of beamline 10.3.2; and investigating natural organic carbon interactions with mineral grains using the STXM (11.0.2).

The program also serves the general environmental synchrotron user community through coordination of resources across the four DOE-supported synchrotron user facilities (ALS, NSLS, and SSRL). By frequent communication with environmental scientists at the other three sources, the ALS program is able to help identify the most appropriate facility for a given investigation across the entire DOE synchrotron complex, and therefore maximize the scientific output of these facilities.

In addition, the program is also working to increase the total amount of beam time available at the ALS through leading the design and construction of a new FTIR beamline that will have greater photon flux (~2x) compared to the existing FTIR beamline.

Using the newly developed FTIR environmental bioreactor, we were able to directly observe the alterations in two common iron oxides under microbial-induced reduction. Figure 1 shows the FTIR spectrum of a hematite film, which is originally very crystalline, as represented by the sharp distinct peaks seen in the magneta spectrum. This film is then coated with ferrihydrite, which adds a broad diffuse baseline to the spectrum but does not alter the position of the original hematite peaks (red). After 17 days of reaction with dissimilatory iron-reducing bacteria (DIRB), the signal from ferrihydrite has been significantly reduced, as a result of both flow-mediated erosion of the ferrihydrite layer and also of recrystallization of the ferrihydrite. A shoulder peak at ~615 cm^{-1} appears, which is consistent with the formation of goethite, and there is a significant shift and broadening of the hematite peaks at ~543 cm^{-1}, ~444 cm^{-1}, and ~305 cm^{-1}, which is indicative of an increase in disorder in the hematite as a result of hydration and/or reductive dissolution.

RELATED PUBLICATION

Neiss, J.; B.D. Stewart, P.S. Nico, and S.E. Fendorf, Speciation-dependent microbial reduction of uranium within iron-coated sands under dynamic flow. Environ. Sci. and Technol. (in press), 2007.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Program, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Development of Highly Heterogeneous Zones of Microbial Activity During Enhanced Bioremediation

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RESEARCH OBJECTIVES

In situ bioremediation of contaminated aquifers through the addition of a carbon source to stimulate biological activity has been demonstrated to be a viable method for cleaning up groundwater. Enhanced microbial activity in the area of the injected carbon source creates conditions that have been shown to lead to biodegradation of chlorinated compounds and immobilization of metals. Not well understood, however, is what occurs in the downstream portions of these plumes.

For more than 8 years, organic carbon (initially Na-lactate, followed by whey) has been added to the groundwater at the source of a 3 km long trichloroethene (TCE) plume at the Test Area North (TAN) site of the Idaho National Laboratory. This activity has led to high levels of microbial activity, resulting in anaerobic conditions that have successfully stimulated complete reductive dechlorination of the TCE in the source area of the plume. The purpose of this project is to characterize biological activity in the downstream areas and assess the potential for additional bioremediation of the groundwater in the distal sections of the plume.

APPROACH

As a follow-up to a study of bioremediation conducted during the initial phases of enhanced bioremediation (Song et al., 2002), groundwater samples were collected in a series of monitoring wells extending from an injection well down-gradient in the plume. The compositions of the microbial communities in these samples were analyzed using high-density DNA microarrays (PhyloChips). The isotopic composition of dissolved gases (methane and inorganic carbon) and chlorinated solvents in the samples were also analyzed to assess the level of relevant microbial metabolic processes (methanogenesis, methane oxidation, reductive dechlorination of solvents, aerobic biodegradation of solvents).

ACCOMPLISHMENTS

Anaerobic conditions in the groundwater extend to greater than 150 m down-gradient from the injection well. Within this zone, concentrations of dissolved methane are high (>3 micromolar), whereas nitrate and sulfate concentrations are depleted. Phylochip analyses of microbial communities, in groundwater samples from the anaerobic zone of the plume, have identified a range of aerobic microorganisms, including methane-oxidizing bacteria and anaerobic organisms such as methanogens, sulfate reducers, and anaerobic methane-oxidizing archaea. Large shifts in the carbon isotope ratios of the methane (from -55‰ in the source area to -28‰ in down-gradient wells) confirm that significant microbial methane oxidation is occurring within the largely anaerobic core of the TCE plume (Figure 1). In addition, the isotope compositions of dissolved inorganic carbon (DIC) decreased from values typical of methanogenic activity (>8‰) in the source area to much lower values (<-13‰) in the down-gradient anaerobic wells, as would be expected for high levels of methane oxidation. Down-gradient from the anaerobic core of the plume, where the dissolved oxygen contents of the groundwater have rebounded, there is molecular evidence for methanogenic microorganisms.

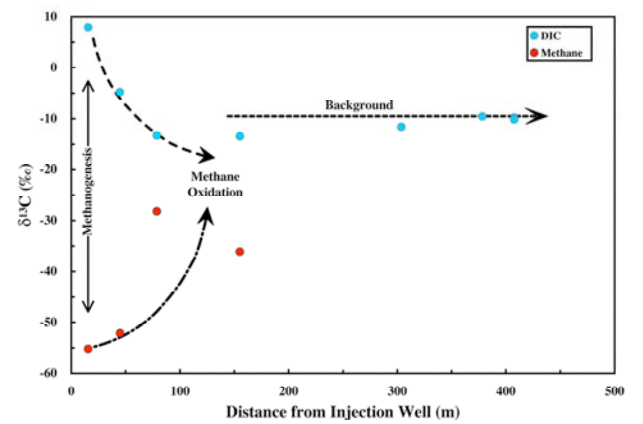

Figure 1. Carbon isotopic compositions of dissolved methane and inorganic carbon in samples from the TAN site plotted versus distance from the injection well. (Both the source area for the TCE and the well into which organic carbon has been added to stimulate microbial activity.) The large increase in the $\delta^{13}C$ of the methane coupled with the drop in the $\delta^{13}C$ of inorganic carbon with distance from the injection well indicate significant methane oxidation occurring within the 150 m of the injection well, despite anaerobic conditions. In the distal portions of the plume, the $\delta^{13}C$ of inorganic carbon returns to background levels.

SIGNIFICANCE OF FINDINGS

These data indicate that diverse microbial communities capable of biodegrading contaminants exist in groundwater, where the groundwater geochemistry may not reflect the conditions thought to be required for some of these communities to be active. This implies that significant biodegradation of contaminants may be occurring in these portions of the plumes.

RELATED PUBLICATION

Song, D.L., M.E. Conrad, K.S. Sorenson, and L. Alvarez-Cohen, Stable carbon isotope fractionation during enhanced *in situ* bioremediation of trichloroethene. Environ. Sci. Technol. 36, 2262–2268, 2002.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Sulfur Isotopes as Indicators of Bacterial Sulfate-Reduction Processes During Field-Scale Uranium Bioremediation

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RESEARCH OBJECTIVES

Aqueous uranium concentrations in a contaminated aquifer in Rifle, Colorado, have been successfully lowered through enzymatic reduction to less soluble U(IV) by acetate-amended microbial activity. The highest U(VI) removal rates are noted during iron reduction and decrease with the onset of sulfate reduction. However, sustained U(IV) attenuation is observed following sulfate reduction and subsequent termination of the acetate amendment. These findings indicate the transition between iron- and sulfate-reducing conditions is an important aspect of the remediation process. Samples collected during a 2006 acetate amendment were analyzed for $\delta^{34}S$ of sulfate and sulfide to explore the utility of sulfur isotopes as indicators of these processes. Objectives of this study include the use of these data to refine the timeline of iron- and sulfate-reduction phases and to determine the stability of sulfide precipitates post-amendment.

APPROACH

Sulfate and sulfide isotopic samples were collected throughout the course of an *in situ* acetate amendment at the DOE Old Rifle Site near Rifle, Colorado. Samples were taken in one background well and three monitoring wells down-gradient of the injection gallery, in conjunction with aqueous geochemical measurements of sulfate, ferrous iron, U(VI), and acetate.

ACCOMPLISHMENTS

Results show an increase of up to 7‰ $\delta^{34}S$ in residual sulfate at the onset of sulfate reduction, followed by a return to background $\delta^{34}S$ values of -8‰ with time. Sulfide $\delta^{34}S$ values of roughly -20‰ at the onset of sulfate reduction increase to background sulfate $\delta^{34}S$ values as sulfate removal approaches 100% and subsequently return to depleted levels following cessation of acetate amendment (Figure 1). Comparable sulfate and sulfide $\delta^{34}S$ values at the height of sulfate reduction suggest total removal of all sulfate accessible to the microbial population. In addition, a steady decline in $\delta^{34}S$ of sulfide, concurrent with increased sulfide concentrations following cessation of acetate amendment, suggests that this increase is not a result of reoxidation of precipitated FeS species. Thus, FeS precipitates formed during the height of sulfate reduction appear to be stable following acetate amendment and may lend to the stability and long-term sequestration of precipitated U(IV).

SIGNIFICANCE OF FINDINGS

This study demonstrates the additional information regarding the transition to sulfate reduction and the fate of sulfide species gained through the use of sulfur isotopes beyond what is obtainable using aqueous geochemical measurements alone. The apparent stability of precipitated sulfide species, indicated by the isotopic data following acetate amendment, is particularly significant in that these species may influence long-term U(VI) sequestration.

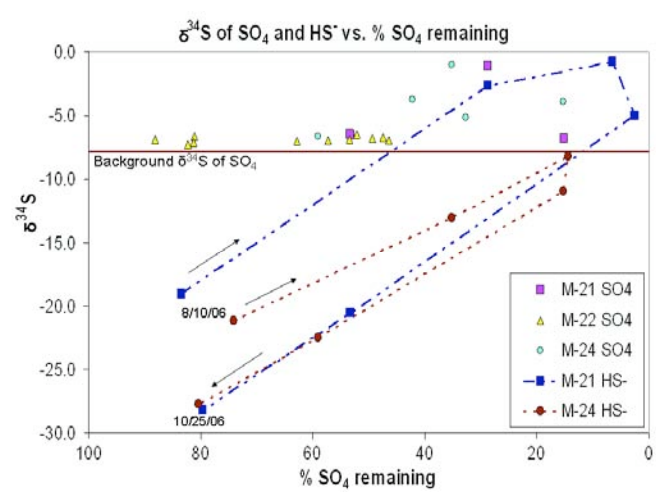

Figure 1. Sulfur isotopes of sulfate and sulfide in three monitoring wells. M-21 is located closest to the injection gallery at 1.5 m down-gradient, followed by M-22 at 3 m and M-24 at 6 m.

RELATED PUBLICATION

Druhan, J.L., M.E. Conrad, K.H. Williams, L. N'Guesson, P.E. Long, and S.S. Hubbard, Sulfur isotopes as indicators of bacterial sulfate reduction processes influencing field-scale uranium bioremediation. Env. Science and Technology (submitted), 2008.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

TRACING ^{99}Tc CONTAMINATION AT THE HANFORD SITE USING THE ISOTOPIC COMPOSITION OF NITRATE

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RESEARCH OBJECTIVES

The Hanford Site in Washington State was used for decades (1940s to the late 1980s) for the production of weapons-grade plutonium, which resulted in significant local radioactive and non-radioactive contamination of the vadose zone and groundwater. Nitrate is a widespread groundwater contaminant at the Hanford Site, with 75 km^2 of the aquifer above the 45 ppm EPA drinking water limit, and locally reaching concentrations of over 1,000 ppm. This contamination came from a variety of sources, including radioactive waste leaking from storage tanks, low-activity waste from site operations released to disposal structures in the ground, and rinsing of naturally occurring nitrate from vadose zone soils. Commonly, groundwater nitrate contamination at Hanford is accompanied by ^{99}Tc (technetium 99), a man-made radioactive isotope with a half-life of 214,000 years. In 2005, during the emplacement of a new groundwater monitoring well (W11-25B) near the WMA-T, high ^{99}Tc and nitrate concentrations were found just below the water table. The ^{99}Tc concentrations, up to 180,000 pCi/L, were much higher than previously observed in nearby wells. Because both nitrate and ^{99}Tc have similar mobility in groundwater, we may also, by placing constraints on the source of nitrate contamination, constrain the source of ^{99}Tc contamination. We have developed an isotopic technique for tracing contaminant nitrate, providing such constraints on the source of the otherwise untraceable mono-isotopic technetium.

APPROACH

The isotopic composition of the nitrogen (δ^{15}N) and the oxygen (δ^{18}O) in nitrate varies depending on the origin of the nitrate. Our previous research has shown that nitrate associated with synthetic nitric acid, nitrate associated with high-activity tank-related waste, and naturally occurring nitrate in the vadose zone each have their own characteristic isotopic signatures, which can be used to trace sources of nitrate contamination. We analyzed groundwater samples taken at discrete depths below the groundwater table in the well with the very high ^{99}Tc concentrations, as well as groundwater samples from other monitoring wells in the general vicinity, for the isotopic composition of nitrate.

ACCOMPLISHMENTS

The results of our groundwater nitrate isotopic analyses are presented in Figure 1. Most of the WMA-T groundwater samples (purple circles) form an array stretching from the field representing synthetic nitrate to the field representing natural background nitrate. The high δ^{18}O end of this array is represented by samples with very high (>900 ppm) nitrate concentrations. Samples at the low δ^{18}O end of the array have the lowest nitrate concentrations. These observations suggest that samples on this array represent mixing between synthetic nitrate and natural nitrate rinsed from the vadose zone. The depth discrete samples from Well W11-25B form a separate array (green squares), indicating mixing between synthetic nitrate and tank-related waste (with high ^{99}Tc content), possibly associated with a major tank leak in 1973.

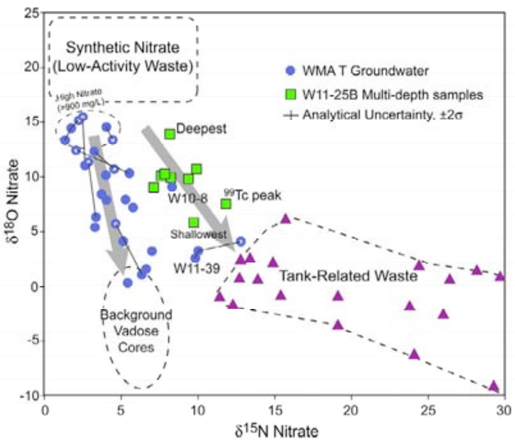

Figure 1. Plot of δ^{15}N vs. δ^{18}O for nitrate in groundwater samples from the vicinity of the WMA-T and for the sub-water table depth discrete samples from W11-25B. Additional data, the field for background cores, and data for tank-related waste from contaminated cores from Singleton et al. (2005). The field for synthetic nitrate (representing low-activity waste) is from Kendall (1998) and Amberger and Schmidt (1987). Lines connect samples from the same well taken at different times, with the more recent sample indicated by a white dot.

SIGNIFICANCE OF FINDINGS

Our results demonstrate the power of isotopic tracking of contaminant nitrate and its co-contaminants, which have provided valuable constraints on the origin of significant ^{99}Tc contamination of groundwater near the WMA-T at the Hanford Site.

RELATED PUBLICATION

Christensen, J.N., M.E. Conrad, D.J. DePaolo, and P.E. Dresel, Isotopic studies of contaminant transport at the Hanford Site, Washington. LBNL-61935. Vadose Zone Journal 6, 1018-1030, 2007.

ACKNOWLEDGMENTS

This work was supported through the Hanford Remediation and Closure Science Project, funded through DOE Richland and by the Assistant Secretary of the Office of Environmental Management, Office of Science and Technology, under the Environmental Remediation Sciences Division, of the Department of Energy, Contract No. DE-AC02-05CH11231 (Berkeley Lab) and Contract No. DE-AC06-76RL01830 (PNNL).

Induced Polarization Monitoring of Microbial Activity During Stimulated Subsurface Bioremediation

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RESEARCH OBJECTIVES

Understanding how microorganisms alter their physical and chemical environment during bioremediation is hindered by our inability to resolve subsurface microbial activity with high spatial resolution. Geophysical methods, such as the induced polarization (IP) technique, have shown promise as sensitive means for delineating regions of stimulated biomineralization. Ongoing research suggests that the IP method may also be sensitive to variations in subsurface geochemical conditions resulting from biological processes, especially when multiple frequencies are utilized. Using an IP monitoring approach, spatiotemporal variations in the development of phase anomalies should reflect the location of active metabolism within aquifer sediments following organic carbon amendment, with the magnitude of the phase response at a given frequency indicative of characteristic metabolic end products, such as aqueous iron and sulfide, or insoluble mineral precipitates.

APPROACH

Surface IP datasets were acquired at multiple frequencies (0.125, 1, and 10 Hz) prior to and at multiple times after the injection of acetate into a uranium-contaminated aquifer near Rifle, Colorado. Differences between the phase and magnitude of the measured potentials relative to the injected current determine the frequency-dependent electrical resistivity of the subsurface. Regions exhibiting a strong frequency-dependence (i.e., those exhibiting a large phase shift) are found to correspond to areas where charge migration by electrolytic transfer in the pore fluid is impeded because of a variety of interfacial conduction mechanisms. These include regions where charge transfer changes from electrolytic to electronic (such as in pore-blocking mineralized rocks) or where grain surface features impede the normal flow of current carrying ions (such as in clay-bearing zones or other areas of high surface charge density). As a result, reactions that alter the way in which electric charge is conducted through the pore space should lead to observable changes in the measured phase response of sediments accumulating electroactive ions and precipitates.

ACCOMPLISHMENTS

We have demonstrated the ability of the IP method to monitor microbe-mediated iron and sulfate reduction during acetate amendment of a uranium-contaminated aquifer near Rifle, CO. During IP measurements, spatiotemporal variations in the phase response between applied and measured voltages correlated with changes in groundwater geochemistry indicative of microbial iron and sulfate reduction and sulfide mineral precipitation. The enhanced sensitivity of the high and low frequency phase responses to accumulated aqueous iron and sulfide, respectively, provide the ability to discriminate the dominant subsurface biogeochemical process. The spectral effect was verified and calibrated using a biostimulated column experiment containing Rifle sediments and groundwater. Sediments and fluids recovered from regions of the field site exhibiting an anomalous phase response were enriched in sorbed Fe^{2+} and cell-associated 2-4 nm diameter FeS nanoparticles. These mineral precipitates and accumulated electroactive ions altered the ability of pore fluids to conduct electrical charge, accounting for the IP response. The results reveal the usefulness of multi-frequency IP measurements for discriminating mineralogical and geochemical changes during stimulated subsurface bioremediation.

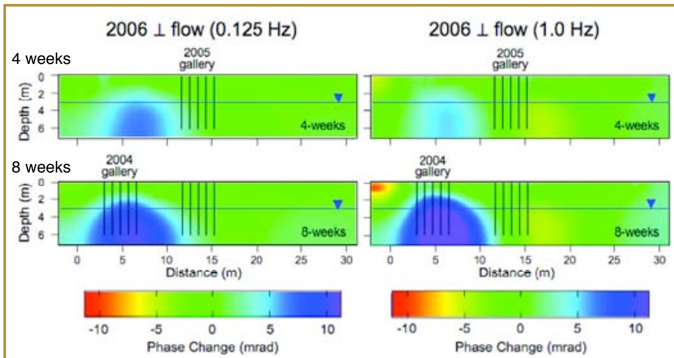

Figure 1. Differential comparison of 2006 surface IP inversion results acquired perpendicular to flow at two frequencies. The results were obtained by subtracting the data obtained after four and eight weeks from the baseline data. The magnitude of the anomalous-phase response was greater at 0.125 than 1 Hz after four weeks, with the opposite trend observed after eight weeks.

SIGNIFICANCE OF FINDINGS

These findings suggest that the spectral IP method represents a minimally invasive means for monitoring stimulated microbial activity within aquifer sediments, with frequency-dependent phase anomalies characteristic of iron and sulfate reduction.

RELATED PUBLICATION

Williams, K.H., A. Kemna, M. Wilkins, J. Druhan, E. Arntzen, L. N'Guessan, P.E. Long, S.S. Hubbard, and J.F. Banfield, Geophysical monitoring of microbial activity during stimulated subsurface bioremediation. Environmental Science & Technology (in preparation), 2008.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Geophysical Monitoring of Stimulated Subsurface Bioremediation Using the Self-Potential Technique

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RESEARCH OBJECTIVES

There is growing interest in the use of geophysical methods to track the products of subsurface microbial activity during stimulated subsurface bioremediation. Among such methods, the self-potential (SP) technique has shown promise as an inexpensive yet sensitive means for delineating variations in subsurface geochemical conditions resulting from biological processes. Interpreting the SP response within the context of a galvanic model makes it possible to use time-varying voltage anomalies to monitor geochemical changes induced by the stimulation of microbial activity. As a result, spatiotemporal variations in the onset, sustenance, and relaxation of the SP anomalies should reflect the location of active metabolism within aquifer sediments following organic carbon amendment. Such variations thus offer an indirect means for verifying geochemical conditions conducive to the removal of soluble contaminants, such as uranium.

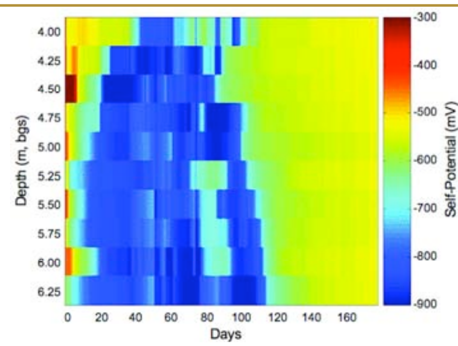

Figure 1. Self-potential data acquired 2.5 m down-gradient from the region of acetate amendment. The depth to each measurement electrode and the time elapsed since the start of acetate injection are shown on the vertical and horizontal axes, respectively, with the color bar representing the magnitude of the self-potential signal. The measured potentials over the first 90–115 days were reflective of sulfate-reduction and corresponded to sulfidic conditions in the vicinity of the measurement electrodes; acetate injection was halted on Day 68, with levels falling below detection by Day 84.

APPROACH

Under conditions in which the measurement and reference electrodes are located in geochemically distinct redox environments, SP anomalies have been shown to be the result of electrochemical reactions involving the electrodes themselves. When bridged through a measuring voltmeter, electrodes located in the electrochemically distinct regions constitute a galvanic cell, generating a voltage potential that persists as long as the concentration gradient is maintained. Charge balance is maintained via electrolytic conduction through the pore space, which also acts to complete the overall circuit. Under conditions in which the geochemical environment directly interacts with the electrode surface, the electrode composition will determine the nature of the measured half-cell reaction. As a result, the magnitude of SP anomalies may be quantitatively interpreted in the same manner as voltages that result when using an ion-selective electrode, albeit over a scale of meters rather than millimeters.

ACCOMPLISHMENTS

We used the SP method to track the onset and persistence of the activity of sulfate-reducing bacteria in a uranium-contaminated aquifer following acetate amendment. Anomalous voltages approaching 900 mV were measured between copper electrodes emplaced within the aquifer sediments and a single $Cu/CuSO_4$ reference electrode located at the ground surface. Onset of the voltage anomalies correlated in time with both the accumulation of dissolved sulfide and the removal of uranium from groundwater. The anomalies persisted for 45 days after acetate injection had ceased, indicative of ongoing sulfate reduction. Geochemical data confirm that anomalous SP voltages and continued sulfate reduction correlated with the sustained removal of uranium. Current-voltage and current-power relationships between measurement and reference electrodes exhibited a galvanic response, with current flow between the two electrodes yielding a steady-state power density of 10 mW/m^2 during the period of sulfate-reduction. Thus, we infer that the SP anomalies resulted from electrochemical differences that developed between geochemically reduced regions and areas having higher oxidation potential. Following the period of sulfate reduction, SP voltages ranged from 500 to 600 mV and were associated with elevated concentrations of ferrous iron in the vicinity of the measurement electrodes. Within 10 days of the voltage decrease following the depletion of sulfide, uranium concentrations rebounded from 0.2 to 0.8 μM, a level still below the background value of 1.5 μM.

SIGNIFICANCE OF FINDINGS

These findings demonstrate that SP measurements provide a minimally invasive means for monitoring stimulated microbial activity within aquifer sediments and verify that redox conditions remain favorable for the stability of bioimmobilized contaminants, such as uranium.

RELATED PUBLICATION

Williams, K.H., S.S. Hubbard, and J.F. Banfield, Galvanic interpretation of self-potential signals associated with microbial sulfate-reduction. LBNL-63396. Journal of Geophysical Research—Biogeosciences, 112, 2007.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

A Statistical Framework for Monitoring Biogeochemical Transformations Using Time-Lapse Geophysical Data

Jinsong Chen and Susan Hubbard
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RESEARCH OBJECTIVES

Bioremediation treatments are used to facilitate reactions that degrade or immobilize contaminants *in situ*, so that they become less hazardous to human and ecological health. These treatments typically result in biogeochemical transformations, such as the formation of precipitates, gas bubbles, and biofilms. Conventional borehole methods limit our ability to monitor such transformations at sufficiently high spatial resolution at field-relevant scales. Although time-lapse geophysical methods have the potential to provide information at the scale and resolution that help us to better understand bioremediation processes, several obstacles hinder the quantitative use of time-lapse geophysical techniques for such purposes. Examples of those challenges include the incomplete understanding of how geophysical attributes respond to biogeochemical transformations, non-uniqueness of relations between the produced biogeochemical transformation products and the recorded geophysical attributes, and scale discrepancies among geophysical and biogeochemical measurements. The goal of this research is to develop a general framework that tackles some of these challenges, and that can be used to provide quantitative estimates of biogeochemical transformations associated with remedial treatments using time-lapse geophysical data. Here, we focus on formulating the framework to estimate a particular transformation that occurs during sulfate reduction processes, using time-lapse seismic and induced polarization datasets.

APPROACH

We develop state-space Bayesian models and use Markov chain Monte Carlo sampling methods to quantitatively estimate the volume fraction and mean grain-size of iron and zinc sulfides commonly formed as a system is reduced via biostimulation. We use a patchy saturation model to relate the seismic data and the Cole-Cole model, together with empirical relations to relate the induced polarization (IP) data to the precipitate properties. The developed framework is applied to a geophysical dataset collected during a laboratory-scale biostimulation experiment (Williams et al., 2005). Figure 1 illustrates the use of the developed method with the laboratory seismic and IP time-lapse datasets, to estimate the evolution of the iron sulfide precipitates as a function of time after biostimulation was initiated.

ACCOMPLISHMENTS

The developed methodology has several favorable characteristics: (1) it is integrated, so that we can combine multiple types of geophysical data sets simultaneously; (2) it is flexible, so that we can explore the effects of different types of prior information for the estimation; and (3) it is robust, so that we can obtain uncertainty information as well as the estimates of quantities of interest.

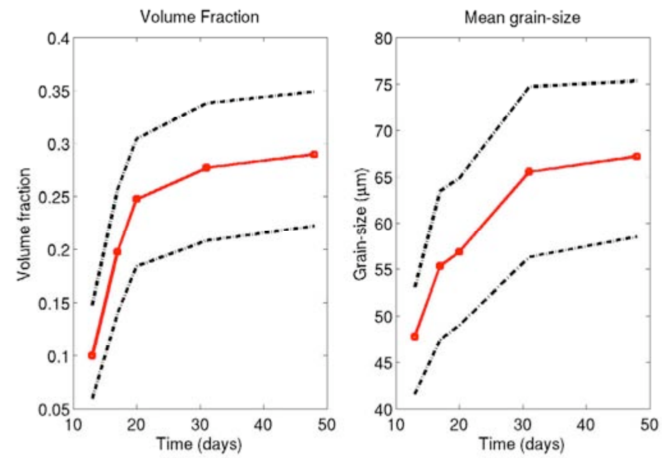

Figure 1. Estimated volume fraction and mean grain-size of precipitates using induced polarization and seismic data. The red lines are the medians of the estimated posterior probability density functions, and the black dashed lines are their corresponding 95% predictive intervals.

SIGNIFICANCE OF FINDINGS

We have developed the first estimation framework that permits quantitative estimation of biogeochemical transformations using time-lapse geophysical datasets. This advance is expected to significantly improve our ability to remotely monitor changes that occur as a system is remediating, which can be used to guide and assess the efficacy of remedial treatments.

RELATED PUBLICATIONS

Chen, J., S. Hubbard, K. Williams, S. Pride, and L. Slater, A statistical framework for monitoring the evolution of precipitates associated with contaminant remediation using time-lapse geophysical data. Water Resources Research (in preparation), 2008.

Chen, J., S. Hubbard, and A. Kemna, A comparison between deterministic and stochastic inversion methods for Cole-Cole model parameters using induced polarization data. Geophysics (in press), 2008.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Development and Application of an Approach for Interpreting Breakthrough Curves Associated with Complex Tracer Injections

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RESEARCH OBJECTIVES

Bromide breakthrough data were collected in conjunction with a biostimulation experiment that was performed at the U(VI) contaminated DOE Rifle Site in Colorado. Several factors contributed to a temporal variability in the bromide injection rate (Figure 1a), including changes in injection rate, injection concentrations, and the injection area. To interpret the bromide breakthrough data in terms of hydrological heterogeneity, we needed to account for the temporal variations in the injection rate. The objective of this study was to develop a method for interpreting breakthrough curves associated with complex tracer injection functions, and to apply the methodology to the Rifle bromide tracer test datasets.

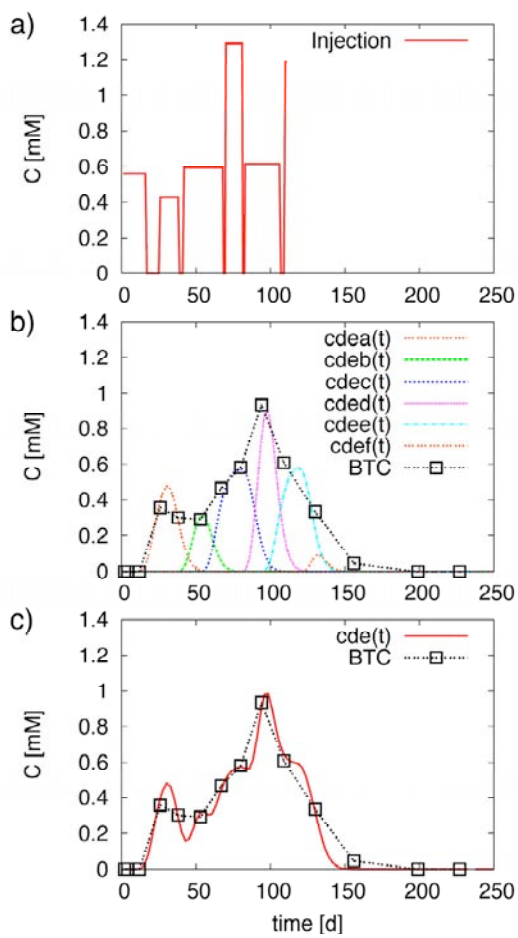

Figure 1. Application of analytical solutions of the one dimensional convection dispersion equation in the presence of a complex injection function: (a) complex injection function, (b) breakthrough curve (BTC) together with CDEs for every step in the injection function, and (c) fit of the superimposed individual CDEs together with the BTC.

APPROACH

Transport processes in the subsurface can be described by the convection dispersion equation (CDE). For one-dimensional transport processes, the CDE can be solved analytically. Although transport in the subsurface is a three-dimensional process, it can be represented as a bundle of 1-D transport processes. This representation permits the 1-D analytical solution of the CDE to be applied to 3-D field tracer tests. Here, we expand this approach to permit interpretation of complex, temporally variable injection functions based on superposition of several 1-D dimensional convection dispersion equations.

ACCOMPLISHMENTS

We applied our approach to the Rifle tracer test datasets. For each of the six steps in the injection function (Figure 1a), we invoked a 1-D convection dispersion equation. Figure 1b illustrates the application of six different CDEs and their relationship to the measured breakthrough curve (BTC). As is shown in Figure 1c, the superposition approach enabled us to capture the complex features of the breakthrough curve at the Rifle site.

SIGNIFICANCE OF FINDINGS

Although tracer tests are often accompanied by complex injection functions, these variations are often not taken into account, which can confound interpretation of the hydrological heterogeneity. The developed approach is significant in that it permits the quantitative characterization of transport processes in the presence of complex injection functions.

RELATED PUBLICATION

Englert, A., S. Hubbard, K. Williams, J. Chen, J. Peterson, A. Kemna, F. Spane, D. Newcomer, and P. Long, Hydrogeophysical field characterization at the DOE Old Rifle site, CO. Eos Trans. AGU, 88(23), Jt. Assem. Suppl., Abstract H31F-05, 2007.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Exploring the Impact of Stimulated Bioremediation on Flow Characteristics

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RESEARCH OBJECTIVES

Many remediation approaches that are being implemented at contaminated subsurface sites induce biogeochemical transformations. Although not yet well quantified at the field scale, these transformations have the potential to alter flow characteristics, which could in turn impact the ability to introduce treatment into the subsurface (via injection) or to withdraw groundwater (via pumping). Here, we interpret bromide tracer test datasets associated with two biostimulation experiments, which were performed in 2002 and 2003 in a flow cell at the DOE Old Rifle Site in Colorado. The biostimulation experiments were intended to facilitate iron and sulfate reduction, which at this site was expected to result in the formation of FeS precipitates. We interpret the datasets in terms of flow velocities, and explore how the velocities vary in space and change over time in response to biogeochemical transformations, such as the generation of precipitates.

APPROACH

Natural gradient bromide tracer test data were collected during the 2002 and 2003 stimulated bioremediation experiments, using 20 injection wells and 15 monitoring wells. To estimate the heterogeneity of transport characteristics using the collected datasets, we invoked a stream tube model, which assumes that the 3-D transport process can be represented by of a bundle of 1-D convective dispersive processes. This approach permits characterization of the transport process in terms of averaged velocity and dispersivity along individual stream tubes.

ACCOMPLISHMENTS

The results of the stream tube analysis, shown in Figure 1, indicate that there is clear spatial variability in the velocity fields, and that the field transitions over time towards lower velocities close to the injection wells and higher velocities further away from the injection wells. The changes in velocity appear to be related to the potential biogeochemical transformations associated with the stimulation, such as iron sulfide and calcite precipitation. Comparison of the velocity field with aqueous geochemical data, collected during the stimulation experiments, in turn suggests that the flow characteristics influenced the spatiotemporal distribution of the biogeochemical transformations.

SIGNIFICANCE OF FINDINGS

The present study is, to our knowledge, one of the first field experiments to illustrate changes in flow characteristics associated with a remedial treatment. Since the heterogeneity of the flow velocity controlled the supply of the biostimulation amendments, the hydrological heterogeneity (and changes thereof) appears to have influenced the spatiotemporal distribution of the biogeochemical transformations. This study suggests that more research is warranted to examine the feedbacks between hydrological heterogeneity and biogeochemical transformations under dynamic conditions.

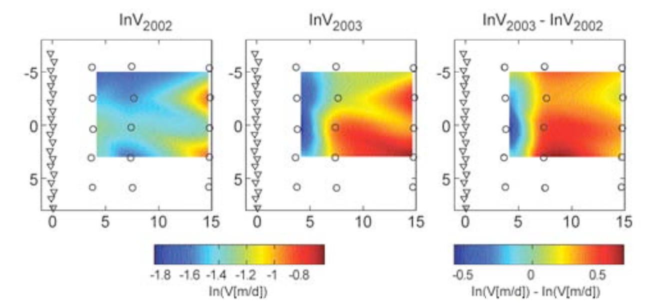

Figure 1. Flow velocity fields associated with the 2002 (left) and 2003 (middle) biostimulation experiment, and the difference between these velocity fields (right), inferred from breakthrough curves at the Old Rifle Site in Colorado. In each of the figures, the injection wells are shown as open triangles, while the downstream injection wells are shown as open circles.

RELATED PUBLICATION

Englert, A., S. Hubbard, K. Williams, J. Chen, J. Peterson, A. Kemna, F. Spane, D. Newcomer, and P. Long, Hydrogeophysical field characterization at the DOE Old Rifle Site, Colorado. Eos Trans. AGU, 88(23), Jt. Assem. Suppl., Abstract H31F-05, 2007.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Inversion of Tracer Data to Quantify Bioremediation-Induced Changes in a Contaminated Aquifer

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RESEARCH OBJECTIVES

Bioremediation techniques aiming to immobilize groundwater contaminants or reduce their toxicity appear to have great potential. There remains, however, a great deal of uncertainty in their application at the field scale, owing to the presence of heterogeneity, both hydrological and geochemical. Hydrological properties are especially important to characterize because they affect how amendments are delivered to contaminated regions of an aquifer. Furthermore, hydrological properties may be in turn affected by biogeochemical transformations during the bioremediation process itself. For example, a remediation technique for immobilizing hexavalent uranium in groundwater involves the stimulation of an iron-reducing bacteria species with an acetate amendment. By-products of the associated reactions, such as precipitation of iron sulfide, could conceivably reduce porosity and permeability. The overall objective of this research is to better understand how transformations associated with bioremediation affect hydrological properties, and vice versa, and whether such changes may be quantified using time-lapse hydrological data.

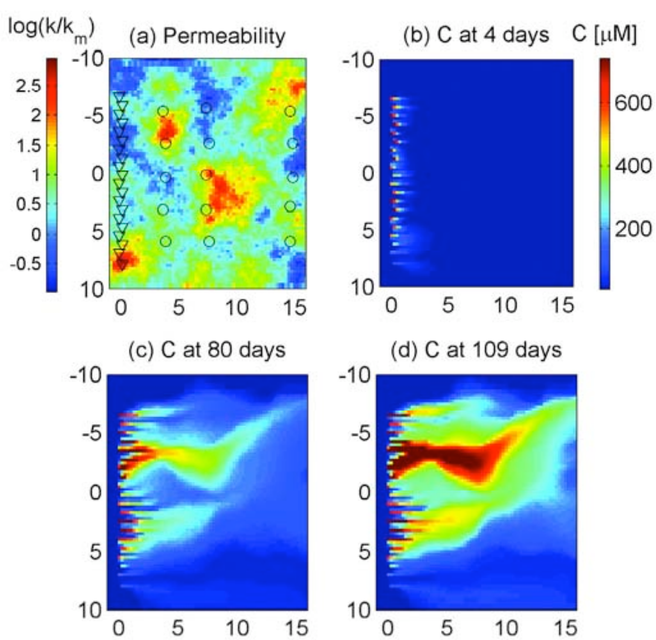

Figure 1. (a) Example permeability distribution obtained by inversion of the 2003 data, and the corresponding simulated distribution of the bromide tracer at several times (b–d). Injection and monitoring wells are represented by triangles and circles, respectively, in (a).

APPROACH

The Old Rifle UMTRA field site in Western Colorado has been the subject of a number of bioremediation experiments that were performed in conjunction with hydrological, geochemical, and geophysical measurements. We consider data from two experiments that were conducted in 2002 and 2003, respectively, in which an acetate amendment, along with a bromide tracer, were delivered into the shallow unconfined aquifer through an injection gallery consisting of 20 closely spaced wells. For each experiment, bromide concentrations were measured in 15 down-gradient monitoring wells as a function of time. Here we aim to use the measured bromide concentrations to estimate the permeability distributions for both experiments using iTOUGH2, a code that provides inverse modeling capabilities to the flow simulator TOUGH2.

ACCOMPLISHMENTS

We developed a depth-averaged 2-D model that allows for inverse modeling of the bromide tracer data at the site. Bromide and water are injected into 20 wells according to the measured time-varying rates and accounting for the fluctuating aquifer thickness. A geostatistical parameterization of the permeability field was implemented using parameters that were inferred from borehole data, reducing the number of unknowns in the inverse problem (to 25 permeability values at selected pilot point locations). A permeability distribution obtained by inversion of the 2003 data and the corresponding simulated distribution of bromide at several times are shown in Figure 1, revealing complex tracer transport in the aquifer. Preliminary results indicate that permeability reduction occurred from 2002 to 2003 in some regions, suggesting that the stimulated bioremediation influenced the hydrological properties at the site.

SIGNIFICANCE OF FINDINGS

The proposed approach is able to capture the spatial heterogeneity of hydrological properties (without requiring direct hydraulic testing), allowing for better understanding of how hydrological heterogeneity changes in response to biogeochemical transformations in an aquifer undergoing bioremediation.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Multiscale Hydrogeophysical Data Integration for Parameterization of Dual-Domain Transport Model at Savannah River Site

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RESEARCH OBJECTIVES

We are developing a multiscale characterization approach that integrates various data types, collected at differing measurement scales, to improve transport predictions at the Savannah River Site. The approach uses surface-based and cross-borehole-based geophysical data, and wellbore data to provide input for a site-wide dual-domain transport model. The dual-domain transport model, also being developed in the characterization effort, incorporates the key interactions between mobile and immobile regions that are expected to play a role in long-term plume evolution.

APPROACH

Analysis of existing characterization data suggests that the study site can be described by two hydrofacies, with one that is on average more mobile than the other, and that these hydrofacies are related to two lithofacies (L=0 and L=1, respectively). A statistical model is used to estimate the unknown proportion of lithofacies (F_I) in each pixel I and the unknown lithofacies type (L_i) in each pixel i, given the following data sets: (1) large-scale surface-based geophysical data; (2) small-scale cross-borehole geophysical data; and (3) small-scale wellbore data, such as from geophysical logs, flowmeter logs, or core samples. An example of the data sets and unknowns that we consider is depicted in Figure 1. Using a Bayesian framework, we derive a conditional probability distribution of the unknown variables (F_I and L_i) for all of their respective pixel locations. The resulting distribution depends on (for the example shown in Figure 1) the probability distribution of the large-scale geophysical data given the unknown values of F_I; the probability distribution of F_I given the unknown values of L_i; and the probability distribution of unknown L_i given the small-scale cross-borehole and wellbore data. The Markov-Chain Monte Carlo (MCMC) sampling method is used to efficiently draw samples from the conditional probability distribution, so that the probability distributions of the unknowns can be inferred.

ACCOMPLISHMENTS

We are currently applying the approach to synthetic data and petrophysical relationships that are representative of site conditions. The approach is being modified, as needed, based on ongoing collection and reduction of multiscale hydrological and geophysical data, and on the evolving characterization objectives that are identified during development of the site-wide transport model. Once refined, the multiscale approach will be used to characterize the relevant field-scale properties at the study site and to parameterize the transport model.

SIGNIFICANCE OF FINDINGS

This approach expands the scale of hydrogeophysical investigations, traditionally restricted to local-scale regions between closely spaced boreholes (~10 m), to site-wide scales that are relevant for modeling plume fate and transport.

RELATED PUBLICATIONS

Chen, J., S. Hubbard, Y. Rubin, C. Murray, E. Roden, and E. Majer, Geochemical characterization using geophysical data and Markov Chain Monte Carlo methods: A case study at the South Oyster Bacterial Transport Site in Virginia. Water Resources Research, 40, W12412, doi: 10.1029/2003WR002883, 2004.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division of the U.S. Department of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

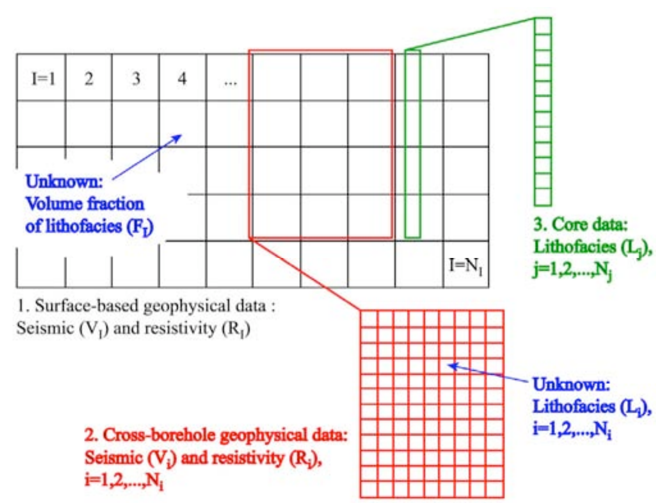

Figure 1. Example of data sets and unknowns considered in multiscale approach. A statistical model is used to estimate the unknown proportion of lithofacies (F_I) in each large-scale pixel I, and the unknown lithofacies type in each small-scale pixel i, given the following data sets: (1) large-scale surface-based geophysical data; (2) small-scale cross-borehole geophysical data; and (3) small-scale wellbore data, such as from geophysical logs, flowmeter logs, or core samples.

Berkeley UXO Discriminator (BUD) for the Detection and Characterization of UXO

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RESEARCH OBJECTIVES

The Berkeley Unexploded-ordnance Discriminator (BUD) is an optimally designed, active electromagnetic system that not only detects but also characterizes unexploded ordnance (UXO). Performance of the BUD system is governed by a target size-depth curve. BUD was designed to detect UXO in the 20 to 155 mm size range for depths between 0 and 1.5 m, and to characterize them in a depth range from 0 to 1.1 m.

APPROACH

The system incorporates three orthogonal transmitters and eight pairs of differenced receivers. BUD is mounted on a small cart to assure system mobility. System positioning is provided by state-of-the-art RTK GPS receiver. The system has two modes of operation: (1) search mode, in which BUD moves along a profile and exclusively detects targets in its vicinity, providing target depth and horizontal location, and (2) discrimination mode, in which BUD, stationary above a target, determines (from a single position) three discriminating polarizability responses together with the object location and orientation.

While UXO objects have a single major polarizability coincident with the long axis of the object and two equal transverse polarizabilities, scrap metal has three different principal polarizabilities. This description of the inherent polarizabilities of a target is a major advance in discriminating UXO from irregular scrap metal. Our results clearly show that BUD can resolve the intrinsic polarizabilities of a target, and that there are very clear distinctions between symmetric intact UXO and irregular scrap metal. Moreover, UXO have unique polarizability signatures, such that distinctions can be made between various UXO.

ACCOMPLISHMENTS

The field surveys at the Yuma Proving Ground in Arizona and Camp Sibert in Alabama showed excellent detection and characterization results within the predicted size-depth range. "Initial blind testing at a controlled site has shown that the BUD performance is significantly above any other system," said Dr. Jeffrey Marqusee, director of the DoD's Environmental Security Technology Certification Program, which administered the Yuma field test.

SIGNIFICANCE OF FINDINGS

BUD has shown that it can differentiate (in real time) buried UXO from harmless metal, as well as determine the location, size, and shape of such potential explosives. This technology can greatly reduce the time and cost of remediation, and potentially provides a valuable, worldwide humanitarian service. Note that BUD received a 2007 R&D100 award for technology advances from *R&D Magazine*.

RELATED PUBLICATIONS

Gasperikova, E., J.T. Smith, H.F. Morrison, and A. Becker, Berkeley UXO discriminator (BUD). LBNL-62263. SAGEEP Proceedings, 1049–1055, 2007.

Smith, J.T., H.F. Morrison, and A. Becker, Optimizing receiver configurations for resolution of equivalent dipole polarizabilities *in situ*: IEEE Trans. Geosci. Remote Sensing, 43, 1490–1498, 2005.

Smith, J.T., H.F. Morrison, L.R. Doolittle, and H.-W. Tseng, Multi-transmitter null coupled systems for inductive detection and characterization of metallic objects: Journal of Applied Geophysics, 61, 227–234, 2007.

ACKNOWLEDGMENTS

This research was supported by the Office of Management, Budget, and Evaluation, of the U.S. Department of Energy under Contract No. DE-AC0205CH11231, and the U.S. Department of Defense under the Environmental Security Technology Certification Program Project No. MM-0437 and Contract No. W74RDV61639913.

Quantifying and Predicting Reactive Transport of Uranium in Hanford Waste Plumes

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RESEARCH OBJECTIVES

Massive quantities (exceeding 85 tons) of U currently residing in the Hanford vadose zone will threaten groundwater and the accessible environment for generations to come. Understanding the status and mobility of this potentially contaminant U in the vadose zone is extremely difficult because of insufficient historical records, sediment heterogeneity, and complexity of the strongly coupled hydrological and geochemical processes. The overall objective of this research is to identify the dominant geochemical reactions and transport processes between waste streams and sediments occurring during seepage and upon aging. This knowledge is important, because the major reactions and transport processes largely determine the current spatial distribution, speciation, and mobility of U within the Hanford plumes.

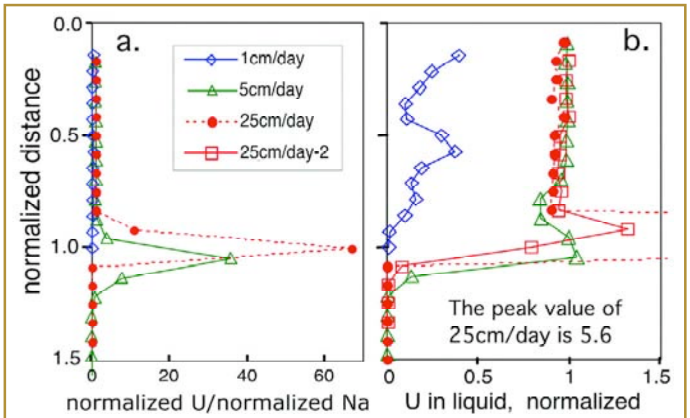

Figure 1. Accelerated U transport and kinetic limitations: (a) Profiles of normalized U:normalized Na, showing U moved faster than Na up to 60 times, and U accumulation at the plume fronts; (b) U profiles normalized to the influent U concentration, showing U concentrations exceeding their source levels by up to 5-fold at the plume front region.

APPROACH

To achieve these goals, we constructed a field-process-based column-profiling method. Using this method, we can study flow and geochemical processes simultaneously. We simulated the Tank BX-102 over-filling event: We synthesized the historical tank waste solution containing extremely high levels of U in alkaline brine, and conducted infiltration experiments, under well-defined conditions, as relevant to the field-release event as possible. Flow rate and aging time were chosen as the main variables in these experiments. Analyses of aqueous and solid phases from these experiments were used to obtain profiles of U concentrations and speciation along the plume paths.

ACCOMPLISHMENTS

Several processes demonstrated in these laboratory experiments have direct relevance to U-contaminated sediments such as those at the Hanford 200 Area. We found that dramatic pH reduction occurred at the plume fronts. Large peak values of Ca^{2+} and Mg^{2+} concentrations were found within plume profiles, resulting from rapid displacement of cation exchange sites by high concentrations of Na^{+}. Maxima in concentrations of these divalent cations, along with pH minima, are indicators of the distance of waste-plume migration. We observed accelerated U transport (faster than the flow); the measured U concentration maxima at plume fronts exceed their source levels by up to 5-fold. Thus, peaks in U concentrations in contaminated sediments can be expected from fast U transport and accumulation at plume fronts. We also found that transport of U in waste plumes was strongly dependent on flow rate. Kinetic limitations on sorption and precipitation permitted practically unretarded U transport at higher flow rates.

SIGNIFICANCE OF FINDINGS

In general, this laboratory study shows that the rate of waste infiltration must have been a primary factor behind the observed deep transport of U in the Hanford vadose zone, and that predictions based on equilibrium K_d partitioning of U would greatly underestimate the extent of U migration. This new understanding of U fate and transport within alkaline waste plumes is important for predicting U current spatial distribution, speciation, and future mobility in the Hanford vadose zone.

RELATED PUBLICATIONS

Wan, J., T. K. Tokunaga, Y. Kim, Z. Wang, R. J. Serne, E. Saiz, and A. Lanzirotti, Effect of saline waste solution infiltration rates on uranium retention and spatial distribution in Hanford sediments. LBNL-63501. Environ. Sci. Technol., 42, 1973-1978, 2008.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Mesoscale Biotransformation of Uranium

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RESEARCH OBJECTIVES

Remediation and long-term stewardship of uranium-contaminated sediments and groundwaters are critical problems at a number of DOE facilities and mining sites. Some remediation strategies based on *in situ* bioreduction of uranium (U) are potentially effective in decreasing U concentrations in groundwaters. Our current research targets three basic issues concerning U bioreduction: (1) effects of organic carbon (OC) forms and supply rates on stability of bioreduced U, (2) roles of iron (Fe) and manganese (Mn) oxides as potential U oxidants in sediments, and (3) microbial community changes in relation to U redox changes.

APPROACH

Our studies are being conducted on U-contaminated sediments from the Field Research Center (FRC), Oak Ridge National Laboratory, in flow-through columns. Transformations of U are being tested in FRC sediments supplied with lactate or acetate at rates ranging from 0 to 580 mM (kg sediment)$^{-1}$ year^{-1}. Micro-x-ray absorption spectroscopy is being used for directly determining distributions of Mn, Fe, and U oxidation states in sediments at various stages of OC-stimulated bioreduction. Chemical methods are being used for determining concentrations of Fe(II), Fe(III), and U in sediments and pore waters. We analyzed the structure of the stimulated microbial communities in columns receiving ten different OC supply treatments at two time points: first during a phase of net U-reduction, and later during a phase of U-reoxidation and remobilization.

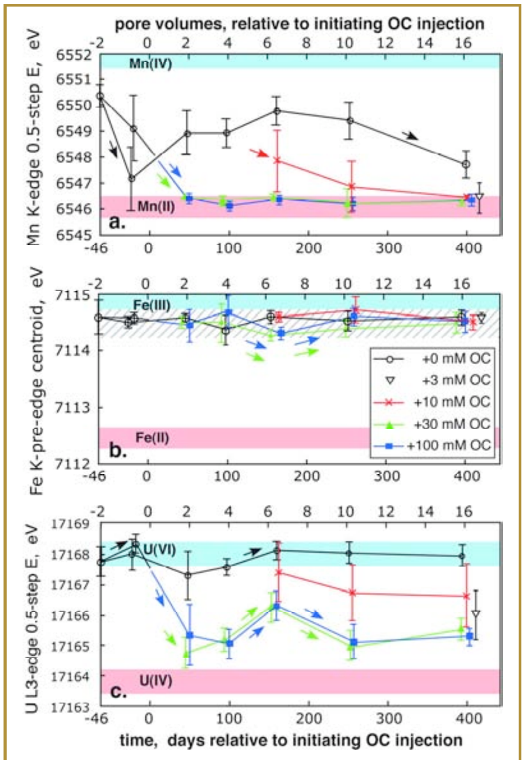

Figure 1. Time trends in average oxidation states, determined by x-ray absorption spectroscopy, of (a) manganese, (b) iron, and (c) uranium in sediments supplied with different concentrations of organic carbon (OC). These results show that, unlike Mn, a large Fe fraction remains unreduced after significant U reduction has occurred.

ACCOMPLISHMENTS

Effluent U concentrations show complex but reproducible dependence on the OC supply rate, consistent with OC oxidation having dual impacts of driving U reduction as well as formation of soluble U(VI)-carbonato complexes. We also found that lactate and acetate have the same geochemical impact on effluent U concentrations, when compared on the basis of C supply rate. We identified several factors that point to a residual reactive Fe(III) fraction in these sediments that likely serves as the terminal electron acceptor for U reoxidation. Community analysis using a high-density 16S microarray (16S Phylochip) indicates that OC supply rate is the primary determinant of the bacterial community composition, and that significant shifts in community dynamics occur between the U-reduction and remobilization phases.

SIGNIFICANCE OF FINDINGS

Organic-carbon-induced U reduction in sediments can exhibit rapid early stage reduction followed by transient U reoxidation. The persistence of high concentrations of Fe(III) supports the possibility that a reactive Fe(III) fraction can drive U reoxidation under reducing conditions. This work also shows that although reoxidized U is eventually further reduced under a continuous supply of OC, a U(VI) fraction remained after over 400 days of reduction.

RELATED PUBLICATION

Wan, J., T.K. Tokunaga, E. Brodie, Z. Wang, Z. Zheng, D. Herman, T.C. Hazen, M.K. Firestone, and S.R. Sutton. Reoxidation of bioreduced uranium under reducing conditions. LBNL-56058. Environ. Sci. Technol. 39, 6162–6169. 2005.

ACKNOWLEDGMENTS

This project is supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Science Program, and Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U. S. Department of Energy under Contract No. DE-AC03-76-SF00098. Use of the Advanced Photon Source and National Synchrotron Light Source was supported by the DOE, Basic Energy Sciences, Office of Science.

In Situ Long-Term Bioimmobilization of CR(VI) in Groundwater Using $\delta^{13}C$-Labeled Slow-Release Lactate

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RESEARCH OBJECTIVES

Our objective in this work is to develop a novel approach and provide evidence of long-term, *in situ* bioimmobilization of Cr(VI) in groundwater, by transformation of toxic and soluble Cr(VI) into nontoxic and insoluble Cr(III) complexes, using a ^{13}C-labeled slow release polylactate.

APPROACH AND METHODS

A $\delta^{13}C$-labeled slow-release polylactate was injected in the Hanford aquifer through the injection well in August 2004. Monitoring was conducted in one upgradient and three downgradient observation wells, using hydrogeological and geochemical measurements (including stable isotope analysis), geophysical measurements, and microbiological analyses of water samples and sediments.

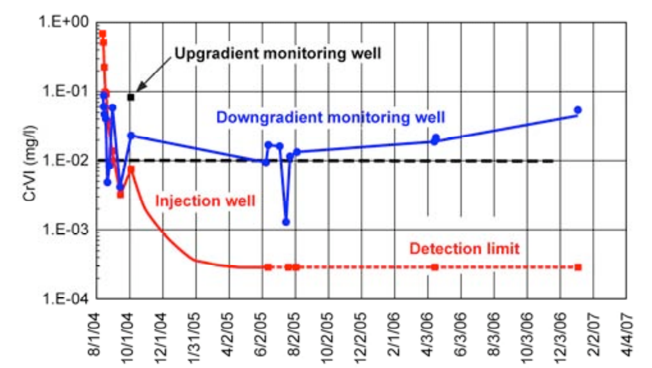

Figure 1. Average Cr(VI) concentrations in water from the injection and monitoring wells.

ACCOMPLISHMENTS

A single lactate injection into Cr(VI)-contaminated groundwater stimulated a 2–3 order of magnitude increase in biomass—up to 10^7–10^8 cells ml^{-1}. The carbon isotope composition of DIC confirmed the presence of lactate metabolism byproducts. Depletion of competing terminal electron acceptors O^2, NO^{3-}, and SO_4^{2-} occurred sequentially, resulting in the creation of dissolved ferrous ion. Sulfate and iron microbial reducers apparently maintain the presence of Fe(II) and hydrogen sulfide, subsequently maintaining Cr(VI) reduction for about 3 years (a) below the drinking water standards in the injection well, and (b) below up-gradient (background) concentration. Prevailing mechanisms of Cr(VI) reduction are direct enzymatic chromate reduction and/or abiotic geochemical processes involving the formation of insoluble complexes of Cr(III) with Fe(II) or S^{-2}.

SIGNIFICANCE OF FINDINGS

Using naturally occurring microorganisms to reduce Cr(VI) is very important for reducing risk of groundwater pollution at contaminated sites. Adding lactate to a contaminated aquifer may offer a low-cost and effective approach to the control of Cr(VI)-contaminated aquifers.

RELATED PUBLICATION

Faybishenko, B., et, el., *In situ* long-term bioimmobilization of CR(VI) in groundwater using slow-release lactate. Environmental Science and Technology (submitted), 2008.

ACKNOWLEDGMENTS

The project has been conducted jointly with PNNL (P.E. Long, D.R. Newcomer, C.T. Resch, K.J. Cantrell) and Regenesis, LLC. This work was supported by the Director, Office of Science, Office of Biological and Environmental Research, Environmental Remediation Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Modeling Biogeochemical Transport of Metals in Mining-Impacted Lake Sediments

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RESEARCH OBJECTIVES

The mobility of metals in riverine, estuarine, and lacustrine sediments is affected by complex coupled biotic and abiotic geochemical processes that reflect redox disequilibrium and cannot be modeled using conventional equilibrium-based models. Competing mechanisms in these environments include the mobilization of sorbed metals by reductive dissolution of hydrous ferric oxides and the precipitation of metal sulfides upon reaction with biogenic sulfide. In addition, the toxicity of metals in polluted environments can have a significant effect on microbial activity and thus indirectly affect metal biogeochemical behavior. The objective of this project was to investigate these processes in the sediments of Lake Coeur d'Alene, Idaho, which have been heavily impacted by upstream mining activities, with emphasis on the reactive-diffusive transport of zinc, lead, and copper.

APPROACH

A conceptual model was developed based primarily on field data and observations reported in the literature. A numerical model was then implemented based upon the PHREEQC code. The model incorporates a multicomponent biotic reaction network, representing multiple terminal electron-accepting processes by a consortium of anaerobic microbial species, via nonlinear kinetics, to capture the electron-acceptor limitations on degradation rates, as well as the inhibition by presence of alternative electron acceptors (Figure 1). In addition, we have constructed and applied "dose-structured" kinetics to quantify the dynamics of microbial populations when their degradation rate is affected by the presence of toxic metals.

ACCOMPLISHMENTS

The model captures the mobilization of metals initially sorbed onto hydrous ferric oxides, through bacterial reduction of ferric iron near the top of the sediment column, coupled with the precipitation of metal sulfides at depth caused by biogenic sulfide production. Key reactions involve the dissolution of ferrihydrite and precipitation of siderite and iron sulfide. The model captures the observed trends of increased alkalinity, sulfide, iron, and heavy metal concentrations below the sediment-water interface, together with decreasing terminal electron-acceptor concentrations with depth, including the development of anoxic conditions within about a centimeter into the sediments.

SIGNIFICANCE OF FINDINGS

This effort provides insights on important biogeochemical processes affecting the cycling of metals in Lake Coeur d'Alene and similar metal-impacted lacustrine environments. In particular, simulation results indicate that the relative rates of ferric iron versus sulfate reduction may be an important factor controlling pH and types of ferrous minerals precipitation at depth. Upon reductive dissolution of hydrous ferric oxides, numerical experiments indicate that a delicate balance takes places between FeS and $FeCO_3$ precipitation, which compete for aqueous ferrous iron, and the formation of aqueous (bi)sulfide complexes, which compete with the precipitation of FeS and other metal sulfides for biogenic sulfide. This study represents a first attempt, to our knowledge, at modeling the reactive transport of heavy metals in sediments by integrating the coupled effects of microbial Fe-oxide reductive dissolution, biogenic sulfide production, and metal sorption through the use of a full surface complexation model under redox disequilibrium.

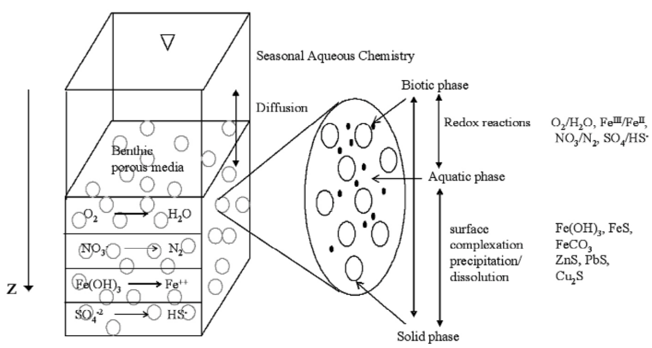

Figure 1. Illustration of the benthic porous media with primary processes governing the fate and transport of toxic metals. Also shown are redox couples and solid phases considered in the biogeochemical model (Sengor et al., 2007).

RELATED PUBLICATIONS

Sengor, S., N. Spycher , T.R. Ginn, R.K. Sani, and B. Peyton B., Biogeochemical reactive-diffusive transport of heavy metals in Lake Coeur d'Alene sediments. Applied Geochemistry, 22, 2569-2594, 2007.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. 0420374, "Metal Toxicity and Microbial Consortia: Response to Acid-Mine Drainage at Lake Coeur d'Alene, Idaho" and by the University of California Toxic Substances Research and Training Program.

Mobility of Tritium in Engineered and Earth Materials

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RESEARCH OBJECTIVES

Fermi National Accelerator Laboratory (Fermilab) operates a neutrino beamline in an underground facility that includes several research halls, a vacuum decay pipe between the beam target and absorber, and various maintenance structures (drainage and ventilation systems, and a walkway). As a byproduct of beamline operation, tritium is produced in engineered materials (i.e., concrete and steel used for shielding) and the surrounding rock. Once the tritium is generated, it may be contained at the source locations or migrate (in the liquid phase or as tritium vapor) to other regions within the facility. The tritium is collected by the drainage system, aired to the atmosphere, contained in engineered materials, or released to the surrounding subsurface environment. The purpose of the study is to better understand the fate and transport of tritium generated in the facility, in order to be able to (1) evaluate potential environmental impacts, (2) determine tritium sources after the beam is shut off, (3) estimate the effects of the planned increase in beam intensity on tritium production and releases, and (4) help design and optimize mitigation measures.

APPROACH

The amount and distribution of tritium present in the facility—and its movement through engineered materials, the fractured rock, and the ventilation and drainage systems—are examined by (1) a detailed analysis of the tritium data collected by Fermilab, (2) laboratory diffusion tests on concrete and rock cores, (3) isotopic analyses of pore-water samples, and (4) numerical simulations of water and air flow and tritium transport.

ACCOMPLISHMENTS

Tritium concentrations in the concrete shielding and the rock formation were measured to determine whether these materials contain sufficient tritium to act as a long-term source. Tritium diffusion coefficients were determined, since they affect the long-term release and uptake of tritium. Using the information from the laboratory experiments and other available data, we developed a model that simulated (1) groundwater flow and tritium transport towards the drainage system, (2) air and water flow through the ventilated walkway and surrounding unsaturated concrete/rock, and (3) tritium vapor transport with the ventilated air and its transfer to liquid water in the surrounding concrete/rock. The main tritium transport mechanisms were identified as (1) advective transport with airflow and mass transfer between gaseous and aqueous phases in underground openings, (2) advective and diffusive transport in concrete and fractured rock, and (3) mass transfer between tritium vapor in the underground openings and concrete or rock walls. The model reproduced the measured tritium concentrations in the drainage water reasonably well.

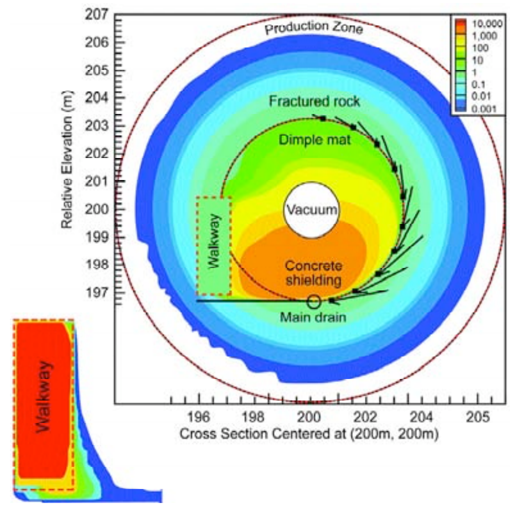

Figure 1. Distribution of simulated tritium concentration (pCi/mL) at 10 years after the beamline is turned off. Tritium is initialized in both the fractured rock and Decay Pipe concrete based on the generated tritium mass pattern. The insert shows the mass transfer between tritium vapor in the walkway and surrounding concrete/rock in terms of relative concentration.

SIGNIFICANCE OF FINDINGS

The combination of laboratory experiments, data analyses, and numerical modeling provided a good understanding of the tritium inventory and transport mechanisms that govern the short- and long-term behavior of this radionuclide. The impact of operational changes on tritium accumulation and release from the facility can be studied, allowing Fermilab to implement appropriate design changes and mitigation measures if necessary.

RELATED PUBLICATION

Finsterle, S., M. Conrad, M. Kennedy, T. Kneafsey, K. Pruess, R. Salve, G. Su., and Q. Zhou, Mobility of tritium in engineered and earth materials at the NuMI Facility, Fermilab. LBNL-61798, Lawrence Berkeley National Laboratory, Berkeley, California, March 2007.

ACKNOWLEDGMENT

This work was supported by the Fermi National Accelerator Laboratory (Fermilab). The support is provided to Berkeley Lab through the U.S. Department of Energy Contract No. DE-AC02-05CH11231.

THE BERKELEY WATER CENTER'S DIGITAL WATERSHED

N. L. Miller, D.A. Agarwal, B.E. Bargmeyer, C. Gu, G.M. Hornberger, S.S. Hubbard, J.R. Hunt, J. Jin, F. Maggi, C.M. Oldenburg, L. Pan, W.J. Riley, N. Spycher, C.I. Steefel, C. Van Ingen, and T. Xu
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RESEARCH OBJECTIVES

It has become increasingly clear that hydrological, meteorological, and biogeochemical processes are coupled and highly dynamic over a wide range of spatial and temporal scales. Understanding these processes with sufficient accuracy, and in the face of anthropogenic and global changes, is a prerequisite to successful management of water resources and ecosystems. Developing such an understanding is predicated on our ability to advance and synthesize relevant but disparate modeling, measurement, analysis, and visualization tools. The Digital Watershed brings together integrative projects that combine engineering, computer science, and ecologic and hydrometeorologic expertise to advance our ability to understand and optimally manage water systems. The Digital Watershed Research Thrust Area currently has three significant projects in its portfolio: Microsoft eScience, NSF/EPA EcoInformatics, and Modeling Framework for Nutrient Cycling.

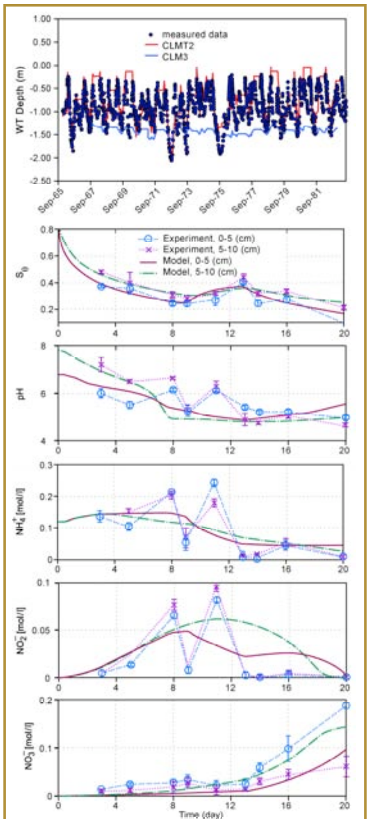

Figure 1. CLM and CLM-TOUGH comparison of the water table with observations (Pan et al. 2007), and experimental and modeled time-evolving average soil water saturation of solutes at 0–5 cm and 5–10 cm (Maggi et al. 2007)

APPROACH AND ACCOMPLISHMENTS

Our eScience project is a partnership between computer and physical science leaders that has developed key infrastructure. This infrastructure includes semi-automated data ingest tools, database and associated schema for data storage, data cubes with pre-defined multidimensional viewing, data browsing, and support for multiple data versions. The project has resulted in an Ameriflux and FLUXNET Scientific Data Server that has received high marks from the biogeochemistry community. The server is being applied to the Russian River watershed as part of an analysis of fish sustainability, in partnership with the National Marine Fisheries Service.

The EcoInformatics project is advancing information-system technology in support of environmental action, science, decision making, and program management. Emerging semantic technologies are enabling us to focus on environmental and health concepts, and the relations between concepts, in ways not previously possible. The research, development, demonstration, and education related to this project serves to advance semantics management and semantics services as needed, to improve the integration of—and the interaction with—the enormous and diverse store of structured, semi-structured, and unstructured data related to the environment and health.

The Modeling Framework for nutrient cycling is a joint BWC-LBNL Earth Sciences Division project supported through the Laboratory Directed Research and Development program. It focuses on enhancing the ability to simulate local-to-regional-scale water, nutrient, and elemental fluxes. The motivation for this effort is the need to predict and interpret the effects of climate, hydrology, and land-use change in areas where such predictions are critical, such as the California Central Valley. The technical objective of the project is the development of a coupled modeling framework (using TOUGH2, TOUGHREACT, and CLM3.0) with reactive biogeochemical transport capabilities (see Figure 1).

SIGNIFICANCE OF FINDINGS

The eScience and EcoInformatics hydrology-ecology-IT projects demonstrate advanced approaches for tackling complex water challenges through integration of advanced data services and IT expertise with hydrological concepts and analysis tools—to efficiently integrate disparate water-related datasets distributed over various scales and forms, in order to test hypotheses regarding water balance, water quality, and ecosystem science questions.

The Modeling Framework for Nutrient Cycling is being used to address the effects of regional climate change on the dynamics of the nitrogen cycle in the Central Valley. This includes simulations of climate forcing on infiltration, vegetation dynamics, microbial processes, chemical reactions, and chemical transport within the near-surface, vadose, and saturated zones. The expected outcome of simulation studies with the new code is a better understanding of water, energy, and nutrient cycling and their changes under various future climate, land-use, and hydrologic scenarios.

RELATED PUBLICATIONS

Gu, C., F. Maggi, G.M. Hornberger, W.J. Riley, R.T. Venterea, C.M. Oldenburg, N.L. Miller, N. Spycher, and T. Xu, Nitrogen losses from different N sources induced by fertilizer application. Water Resources Research (in review), 2008.

Maggi, F., C. Gu, W.J. Riley, R.T. Venterea, G. M. Hornberger, T. Xu, N. Spycher, C.I. Steefel, N.L. Miller, and C.M. Oldenburg, Mechanistic modeling of biogeochemical nitrogen cycling: Model development and application in an agricultural system. Journal of Geo. Res. - Biosciences, 113, 2008.

Pan, L., J. Jin, N.L. Miller, Y-S Wu, and G.S. Bodvarsson, Coupling TOUGH2 with CLM3: Developing a coupled land surface and subsurface model. LBNL-61018, Vadose Zone Journal (in press), 2007.

Coupled Modeling of Hydrology, Nutrient Cycling, and Vegetation: Applications to Agricultural Fields

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RESEARCH OBJECTIVES

The biogeochemical nitrogen cycle and NO, N_2O, and CO_2 gas production in nitrogen-enriched agricultural fields are mediated by several soil microbial populations, the hydrological cycle, plant dynamics, and climate. Understanding the release of NO, N_2O, and CO_2 from the soil surface to the atmosphere is a key factor in controlling greenhouse gas emissions, and assumes ever greater importance in view of the expected increase in biofuel, food, and fiber production. The objective of this research is to develop a mechanistic model for N cycling and losses from agricultural fields, and to investigate the effects on N cycling of irrigation and fertilizer amount, type, and depth of application.

APPROACH

We have developed a mechanistic model (TOUGHREACT-N) based on TOUGH2 and TOUGHREACT for various nitrification and denitrification pathways, multiple microbial biomass dynamics, hydrological dynamics, and chemical reactions at local equilibrium and under kinetic control. The soil column is represented in a 1-D framework, with hydraulic properties described by a water tension/saturation model. Biotic and abiotic reactions are assumed to follow Michaelis-Menten kinetics, while biomass is assumed to follow multiple Monod growth kinetics accounting for electron donor, electron acceptor, and inhibitor concentrations. Water flow is modeled with the Darcy-Richards equation, and advective and diffusive tracer transport is modeled in both gaseous and liquid phases.

ACCOMPLISHMENTS

We have applied TOUGHREACT-N to an agricultural field and tested its performance against measurements of soil moisture, pH, NH_4^+, NO_2^-, and NO_3^- ion concentrations, and NO, N_2O, and CO_2 gas emissions from the soil. Good agreement between field observations and model predictions was found for all these quantities. We have been able to estimate gas emissions, solute leaching of several nitrogen species, and the vertical distribution of nitrifier and denitrifier populations. Finally, we have carried out a comprehensive analysis of gaseous emissions and solute-leaching fractionation and losses for various fertilization and irrigation practices.

SIGNIFICANCE OF FINDINGS

In contrast to the predictions of nonmechanistic, coarse-scale models, all losses nonlinearly increase with fertilizer and water application amount, and with fertilizer application depth (Figure 1). Different fertilizer types have resulted in substantially different N-loss patterns over time, and these patterns depend strongly on soil type. Our results suggest revision of the general assessment of soil N balances and N loss estimates from field to watershed scales.

RELATED PUBLICATIONS

Maggi, F., C. Gu, W.J. Riley, G.M. Hornberger, R.T. Venterea, T. Xu, N. Spycher, C. Steefel, N.L. Miller, and C.M. Oldenburg, Mechanistic modeling of biogeochemical nitrogen cycling: model development and application in an agricultural system, JGR - Biogeosciences, 13, 2008.

Gu, C., F. Maggi, W. J. Riley, G.M. Hornberger, R.T. Venterea, T. Xu, N. Spycher, C. Steefel, N.L. Miller, and C.M. Oldenburg, Nitrogen losses from different N sources induced by fertilizer application. Water Resources Research (in review), 2008.

ACKNOWLEDGMENT

This work was supported by Laboratory Directed Research and Development (LDRD) funding from Berkeley Lab, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. This research was carried out in collaboration with the Berkeley Water Center.

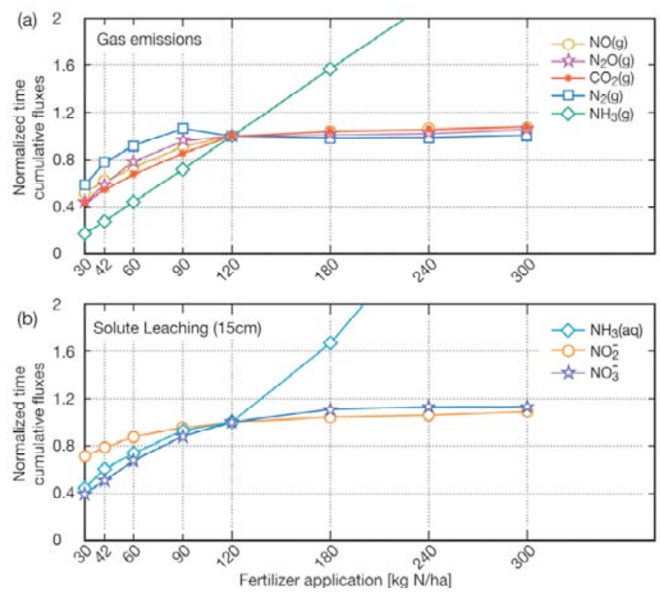

Figure 1. (a) Cumulative normalized gas fluxes and (b) leachate fluxes measured at 15 cm depth as functions of fertilizer amount. Fluxes are normalized to those corresponding to a fertilizer application of 120 kg N ha^{-1}.

Comparison of Two State-of-the-Art Remote-Sensing Techniques for Development of Improved Wetland-Drainage Management Practices

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RESEARCH OBJECTIVES

In response to the looming threat of future water shortages in California, the Department of Interior has required that water contractors develop water conservation plans. The criteria for agricultural and urban water contractors are well established, but there are no equivalent criteria available for seasonally managed wetlands. The ability to estimate water and salinity balances from the 170,000 acres of managed seasonal wetlands in the San Joaquin Basin of California is also critical to management of salt loads in wetland drainage, to improve compliance with stringent Environmental Protection Agency (EPA) mandated water quality objectives for salinity. There is a dearth of data and of analytical tools to quantify the relationships between wetland water and drainage management and ecological health.

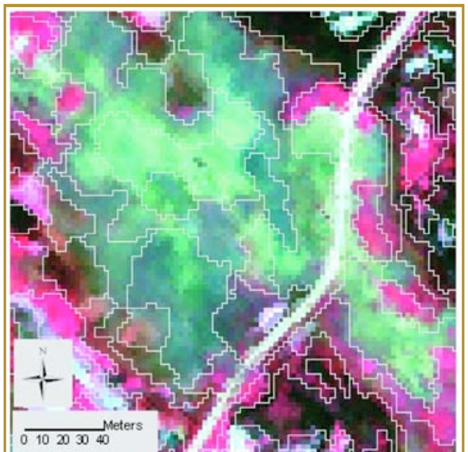

Figure 1. Polygon-based segmentation of high-resolution multispectral imagery of seasonal wetland vegetation into self-similar objects

APPROACH

The most important factors in developing wetland water and drainage management practices are estimates of the composition of wetland moist-soil-plant vegetation, and the water required to meet evapotranspiration losses of the various species of moist soil plants. Polygon-based E-Cognition software—which uses spectral and shape characteristics of the raw high-resolution imagery to separate pixels into self-similar landscape objects—and pixel-based ERDAS imaging software were compared in their ability to accurately map wetland vegetation. A maximum likelihood classifier was selected for analysis of the images. The technique requires the input of training data used to define statistically based spectral bounds for each class. Training areas were derived from ground-truth points by incorporating field data that described the size and shape of the patch within each wetland impoundment, using a modified version of the California Native Plant Society's Rapid Assessment Protocol. Accuracy assessment was performed using 50% of the ground-truth data not used for the development of spectral signatures.

ACCOMPLISHMENTS

Maps of seasonal wetland moist-soil plants in the San Joaquin Basin were developed with a combination of pixel- and polygon-based image processing techniques, using 2-meter Quickbird imagery flown during April, May, and June 2005. Twenty-six different plant communities were represented in a total of 20 land cover classes. An overall mapping accuracy of 60% was achieved, with slightly better overall accuracy achieved using the pixel-based methodology. However, future improved utilization of the information present in high-resolution imagery obtained at different dates, and improved stratification of data collection across land-cover classes, will likely favor the polygon-based method. Characteristic of the complexity inherent in these wetlands, land-cover classes, such as the important waterfowl food source Crypsis schoenoides (swamp timothy), were mapped at an accuracy approaching 80% when combined with a spectrally similar land-cover class Scirpus marititimus (alkali bulrush).

SIGNIFICANCE OF FINDINGS

The results of this research are encouraging for future efforts to map seasonal wetlands throughout the United States. Remote-sensing techniques, such as those compared in this study, make it possible to develop quantitative vegetation assessments from previously unmapped areas that would otherwise be inaccessible or prohibitively costly to survey. Accurate maps of wetland vegetation will lead to the first realistic estimates of regional wetland seasonal evaporation and evapotranspiration—which are important first steps in developing improved water and drainage management practices. Future improvements to the methods developed in this research, using even finer resolution imagery and greater overflight frequency, will be sought through collaborative ventures with the Grassland Water District, the California Department of Fish and Game, and the California Waterfowl Association.

RELATED PUBLICATIONS

Quinn, N.W.T., and W. Mark Hanna, Real-time adaptive management of seasonal wetlands to improve water quality in the San Joaquin River. Advances in Environmental Research, 5, 309–317, Elsevier Science Ltd., 2002.

ACKNOWLEDGMENTS

We are grateful for the support of the Grassland Water District and the California Department of Fish and Game. Funding was provided by the State Water Resources Control Board and the U.S. Bureau of Reclamation.

Impacts of Delayed Drawdown on Aquatic Biota and Water Quality in Seasonal Wetlands

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RESEARCH OBJECTIVES

The 178,000-acre Grassland Ecological Area in California's San Joaquin Valley provides overwintering habitat to waterfowl on the Pacific Flyway. The major management activity is the fall flooding and spring drawdown of wetlands, timed to optimize the availability of forage vegetation and invertebrates for ducks and shorebirds. Wetland drainage contains elevated concentrations of salt, boron, and nutrients, increasing the frequency of water-quality violations in the San Joaquin River (SJR) during dry years. Compliance with SJR water-quality objectives can be achieved by timing wetland drawdown to coincide with the increased assimilative capacity in the river during mid-March to mid-April, when reservoir releases are increased to aid salmon migration.

The present research is part of a large-scale, multiyear investigation by several institutions on the impacts of delayed drawdown on wetland ecology and water quality. The focus of the present research is the algae and invertebrate populations and their effects on water quality. The unknowns addressed are (1) the concentrations of suspended microalgae resulting from delayed drawdown; (2) the relative importance of factors that limit microalgae concentrations, such as invertebrate grazing, nutrients, and turbidity; (3) changes in nutrient and organic matter concentrations in the drainage; and (4) changes in planktonic and benthic invertebrate densities.

APPROACH

To determine the effects of delayed drawdown, three matched pairs of wetland basins (20–100 acres each) were selected for study within the Grassland Ecological Area. In each pair, one wetland has been operated with the traditional March drawdown, while for the other, drawdown has been delayed a month. Water and soil samples have been collected during the flooded period at the inlet and outlet weirs and along transects. The water quality tests have included suspended solids, nitrogen and phosphorus, total organic carbon, alkalinity, and turbidity. Algae and invertebrates have been enumerated and identified to the genus level.

ACCOMPLISHMENTS

The sampling for the first year of the study was conducted during February–April 2007. Suspended microalgae were predominantly chorophytes and diatoms rather than cyanobacteria, and zooplankton were predominantly algae-grazing water fleas *(Daphnia)*. Preliminary analysis shows that despite a general increase in the density of *Daphnia* during the delayed drawdown, microalgae concentrations still increased substantially in two of the three wetlands (150% and 330% increases reaching up to 39 mg/L volatile suspended solids), whereas the concentration declined 47% in the third wetland. The reason for this decline has yet to be determined. Additional analysis and a second year of sampling is planned.

Figure 1. Student Laleh Rastegarzadeh collecting data at the Gadwall-5 wetland outlet, Grassland Water District, California.

SIGNIFICANCE OF FINDINGS

The main purpose of delayed drawdown is to increase the dilution of the wetland drainage salinity in the SJR. The apparent secondary effect of increased invertebrate densities should improve shorebird forage opportunities, but concomitant increases in suspended algae biomass lead to greater organic matter discharges. These competing factors will be considered by wetland managers and regulators as they work to protect wildlife and societal uses of the San Joaquin Valley's water resources.

RELATED PUBLICATIONS

Stringfellow, W. T., and N.W.T. Quinn, Discriminating between west-side sources of nutrients and organic carbon contributing to algal growth and oxygen demand in the San Joaquin River. LBNL-51166, Lawrence Berkeley National Laboratory, Berkeley, Calif, 2002.

ACKNOWLEDGMENTS

We are grateful for the assistance of Refuge Supervisor John Beam and Ricardo Ortega, both of the California Department of Fish and Game. Funding is provided by the UC Salinity/Drainage Program.

Toward Understanding the Relationship Between Groundwater and Hydroclimate over the California Merced River Basin

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RESEARCH OBJECTIVES

Groundwater is a major source of fresh water resources in the western United States. Understanding and forecasting groundwater level changes are essential to the region's well being. The objective of this study is to quantitatively investigate the relationship between the groundwater level and climate variation over the Merced watershed.

	Winter	Spring	Summer	Fall
P	0.38	0.39	0.45	0.16
E	0.10	-0.42	0.45	0.48
R	0.30	0.52	0.15	0.58
SWE	0.54	0.38	-0.23	-0.22
TG	0.12	-0.51	-0.36	0.05

Table 1. Correlations coefficients between water table and precipitation (P), evaporation (E), surface temperature (TG), streamflow (R), and SWE for the 55-year period of 1948–2002. The numbers in italics indicate that the correlation coefficients do not pass the 99% significance test.

APPROACH

This study was performed using the Single Column Climate Model (SCCM) developed by the National Center for Atmospheric Research (NCAR). In SCCM, 18 vertical sigma layers are configured from the surface to the top of the atmosphere, at which the pressure is 1.8 hPa. The study domain has 24 grid cells at approximately 15 km resolution, which covers the entire Merced watershed, and SCCM ran independently at each grid cell. Reanalysis data developed by the National Centers for Environmental Prediction (NCEP)/NCAR were used in the SSCM for the initial and lateral conditions, with the lateral conditions updated monthly. A 55-year simulation was performed over the period of 1948–2002 at each grid cell.

ACCOMPLISHMENTS

The statistical analysis based on the SCCM simulations (Table 1) indicates that the water table is positively correlated with precipitation and snow water equivalent (SWE) during winter. A similar correlation for precipitation and SWE is also seen in spring. In addition, the colder surface is found to lift the water table by suppressing evaporation in this season, while the warmer surface lowers the water table by increasing evaporation. Meanwhile, a positive correlation between water table and runoff is very significant in spring. In summer, the higher (lower) water table produces stronger (weaker) evaporation, which significantly increases (decreases) precipitation. Meanwhile, the stronger (weaker) evaporation results in colder (warmer) surface. The water table in the fall has the same influence on evaporation as in summer, but it is also positively correlated with runoff. However, a relationship between precipitation and the water table is not found in this season, because the impact of surface and shallow subsurface runoff on the water table is very dominant.

FINDINGS

It is shown that the water table is highly correlated to the climate change in all four seasons, but the processes with high correlations are different in different seasons (Table 1). The strongest relationship between the water table and climate change is found in the spring season for this region, indicating that the land-surface processes are most actively interacting with the atmosphere during the this season, as compared to the other three seasons.

RELATED PUBLICATIONS

Pan, L., J. Jin, N.L. Miller, Y.-S. Wu, and G. Bodvarsson, Modeling hydraulic responses to meteorological forcing: From canopy to aquifer. Vadose Zone Journal, 7 (1), 2008.

ACKNOWLEDGMENTS

Support for this work is provided by the California Energy Commission under Grant 500-02-004. Work performed at Lawrence Berkeley National Laboratory is supported under Contract No. DE-AC02-05CH11231.

Drought Analysis of the California Central Valley Surface-Groundwater Conveyance Sysytem

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RESEARCH OBJECTIVES

To provide water-resources decision makers with a better understanding of the consequences of persistent droughts, we have developed a series of numerical investigations to determine system behavior and economic impacts under a range of prescribed drought conditions. The objectives of these investigations are to quantify the impacts of long-term droughts—an analogue for snowpack reduction—on water storage and hydropower generation, and to illustrate the potential for conjunctive use of surface and subsurface storage, in order to limit the adverse impacts of drought and snowpack reduction on water supply and hydropower generation. This includes how groundwater pumping compensates for reductions in surface inflow, the extent to which the water table is reduced, and when this system recovers or reaches a new equilibrium.

APPROACH

Analysis of California Central Valley impacts of sustained droughts are based on a series of specified reductions of 10–70% in net surface flows for periods ranging from 10 to 60 years, and applied to the California Department of Water Resources (CDWR) California Central Valley Simulation Model (C2VSIM). This simplified methodology represents a means by which to evaluate the impact of reductions in net surface inflow to reservoirs. Rather than focus on causes of global climate change, the CDWR Water Plan looks at potential impacts of climate change on water resources in California and strategies for adapting to these changes.

ACCOMPLISHMENTS

Evaluation of the range of reservoir-operating and groundwater-pumping scenarios show how the water table responds to these prescribed droughts, including the rate of groundwater drawdown during drought and the rate of groundwater recovery after drought. Figure 1 (upper) illustrates the relative change in Central Valley water table levels (delwt) in response to the most severe prescribed drought scenario for 60 years. Here, stream flow to major California reservoirs is reduced to 70% below average from 2010 to 2070. Surface irrigation deliveries to agriculture fall to roughly 50% of average deliveries, with farmers assumed to increase groundwater pumping to offset the decline in their surface deliveries. The uppermost panel illustrates groundwater levels with an assumed constant amount of irrigation water applied to agricultural crops. The lower panel assumes that low value crops are removed from production when groundwater pumping ceases to be profitable.

Constant crop-water demand in the Sacramento Basin results in a groundwater decline of 77 feet during the imposed drought, but recovers rapidly. In the Tulare basin (SR17), groundwater drops 390 ft during the drought period, recovering slightly after the drought. The northern Central Valley is better protected from drought than the southern region. The trend of falling groundwater is maintained even after accounting for a decline in high-cost groundwater pumping.

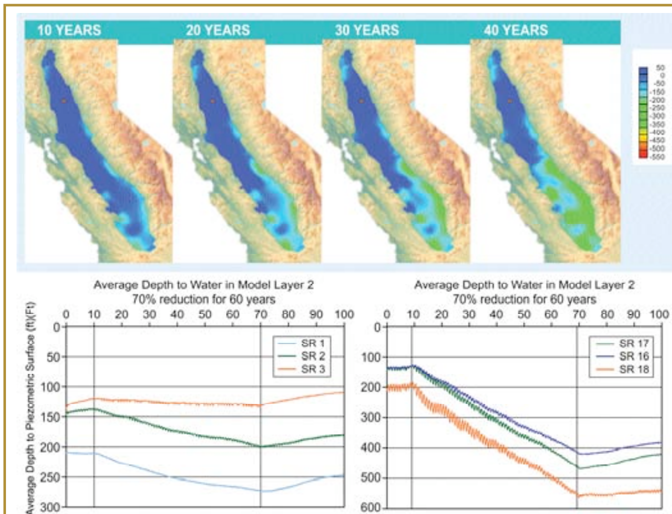

Figure 1. The upper panel shows California Central Valley water table response to a prescribed 70% reduction in surface flow for 10, 20, 30, and 60 years. The 10-year spin-up, surface flow reduction, and 30-year recovery time series for Sacramento Basin subregions, SR1, SR2, SR3, and San Joaquin subregions SR16, SR17, and SR18.

SIGNIFICANCE OF FINDINGS

Our partial, preliminary results show that drought causes groundwater levels to decline throughout the California Central Valley, but the impact on the groundwater table is less severe in the northern than in the southern Central Valley (and groundwater recovery is much quicker). The impact is not severe enough to cause dramatic changes in crop-water demands in either the northern or southern basins.

RELATED PUBLICATIONS

Miller, N.L., L.L. Dale, S. Vicuna, C. Brush, J. Dogrul, and T. Kadir, Drought analysis of the California Central Valley surface-groundwater-conveyance system. Report to the Department of Water Resources, Presentation at the Fall 2006 AGU, J. American Water Resources Association. (in review), 2007.

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